

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In Re the Application of: ) Group Art Unit: 1771  
ABRAMS, Louis Brown )  
Serial No.: 10/614,340 ) Confirmation No.: 7865  
Filed: July 3, 2003 ) Examiner: JUSKA, CHERYL ANN  
Atty. File No.: 4811-16 )  
For: "PROCESS FOR PRINTING AND ) REQUEST FOR CONSIDERATION  
MOLDING A FLOCKED ) OF INFORMATION DISCLOSURE  
ARTICLE" ) STATEMENT FILED FEBRUARY 7, 2005  
) Electronically Submitted

Mail Stop Issue Fee  
Commissioner for Patents  
P.O. Box 1450  
Alexandria, VA 22313-1450

Dear Sir:

On February 7, 2005, Applicant submitted an Information Disclosure Statement in the above-identified patent application. The Information Disclosure Statement was submitted before a first Official Action. The Information Disclosure Statement, including copies of the references cited therein, is attached hereto as Exhibit A.

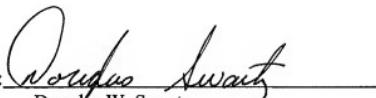
Upon recent review of the file for the above-identified case, Applicant has discovered this Information Disclosure Statement has not been considered by the Examiner.

Applicant hereby respectfully requests that the Information Disclosure Statement of February 7, 2005, be considered by the Examiner.

Although no fees are believed due in connection with this communication, please charge any fees deemed necessary to Deposit Account No. 19-1970. If additional information is required please contact the undersigned.

Respectfully submitted,

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By: 

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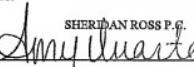
Date: Nov. 15, 2007

# **EXHIBIT A**

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Appl. No. : 10/614,340  
Applicant : ABRAMS, Louis Brown  
Filed: July 3, 2003  
TC/A.U. : 1733  
Examiner:  
Docket No. : 4811-16  
Customer No. : 22442  
Title: "PROCESS FOR PRINTING AND MOLDING A FLOCKED ARTICLE"

Mail Stop Amendment  
Commissioner for Patents  
P.O. Box 1450  
Alexandria, VA 22313-1450

CERTIFICATE OF FACSIMILE TRANSMISSION	
I HEREBY CERTIFY THAT THIS PAPER IS BEING FACSIMILE TRANSMITTED TO THE UNITED STATES PATENT AND TRADEMARK OFFICE TO (703) 872-9306 ON 2-07-2005.	
BY:	SHERIDAN ROSS P.C. 

**NINTH SUPPLEMENTAL INFORMATION DISCLOSURE STATEMENT**

Dear Sir:

The references cited on attached Form PTO-1449 are being called to the attention of the Examiner.

- Copies of the cited non-patent, non-published patent application, and/or foreign references are enclosed herewith.
- Copies of the cited U.S. patents/patent application publications are not enclosed in accordance with the waivers dated July 11, 2003 and October 19, 2004, whereby patent applications filed, regardless of the filing date, need not submit copies of U.S. patents and U.S. patent application publications.
- Copies of the cited references are not enclosed, in accordance with 37 C.F.R. 1.98(d), because the references were cited by or submitted to the U.S. Patent and Trademark Office in prior application Serial No. \_\_\_\_\_ filed \_\_\_\_\_, which is relied upon for an earlier filing date under 35 U.S.C. § 120.
- To the best of applicants' belief, the pertinence of the foreign-language references are believed to be summarized in the attached English abstracts and in the figures, although applicants do not necessarily vouch for the accuracy of the translation.
- Examiner's attention is drawn to the following co-pending applications, copies of which have been or are being submitted:

Serial No. \_\_\_\_\_ filed \_\_\_\_\_

Other: \_\_\_\_\_

Submission of the above information is not intended as an admission that any item is citable under the statutes or rules to support a rejection, that any item disclosed represents analogous art, or that those skilled in the art would refer to or recognize the pertinence of any reference without the benefit of hindsight, nor should an inference be drawn as to the pertinence of the references based on the order in which they are presented.

Submission of this statement should not be taken as an indication that a search has been conducted, or that no better art exists.

It is respectfully requested that the cited information be expressly considered during the prosecution of this application and the references made of record therein.

#### FEES

<input checked="" type="checkbox"/>	<p>37 CFR 1.97(b): No fee is believed due in connection with this submission, because the information disclosure statement submitted herewith satisfies one of the following conditions ('X' indicates satisfaction):</p> <ul style="list-style-type: none"><li><input type="checkbox"/> Within three months of the filing date of a national application other than a continued prosecution application under 37 CFR 1.53(d), or</li><li><input type="checkbox"/> Within three months of the date of entry into the national stage of an international application as set forth in 37 CFR 1.491 or</li><li><input checked="" type="checkbox"/> Before the mailing date of a first Office Action on the merits, or</li><li><input type="checkbox"/> Before the mailing of a first Office action after the filing of a request for continued examination under 37 CFR 1.114.</li></ul> <p>Although no fee is believed due, if any fee is deemed due in connection with this submission, please charge such fee to Deposit Account 19-1970.</p>
<input type="checkbox"/>	<p>37 CFR 1.97(c): The information disclosure statement transmitted herewith is being filed after all the above conditions (37 CFR 1.97(b)), but before the mailing date of one of the following conditions:</p> <ul style="list-style-type: none"><li>(1) a final action under 37 C.F.R. 1.113 or</li><li>(2) a notice of allowance under 37 C.F.R. 1.311, or</li><li>(3) an action that otherwise closes prosecution in the application.</li></ul> <p>This Information Disclosure Statement is accompanied by:</p> <ul style="list-style-type: none"><li><input type="checkbox"/> A Certification (below) as specified by 37 C.F.R. 1.97(e). Although no fee is believed due, if any fee is deemed due in connection with this submission, please charge such fee to Deposit Account 19-1970.</li></ul> <p>OR</p> <ul style="list-style-type: none"><li><input type="checkbox"/> Please charge Deposit Account 19-1970 in the amount of \$180.00 for the fee set forth in 37 C.F.R. 1.17(p) for submission of an information disclosure statement. Please credit any overpayment or charge any underpayment to Deposit Account 19-1970.</li></ul>
<input type="checkbox"/>	<p>37 CFR 1.97(d): This Information Disclosure Statement is being submitted after the period specified in 37 CFR 1.97(c).</p> <ul style="list-style-type: none"><li><input type="checkbox"/> This information Disclosure Statement includes a Certification (below) as specified by 37 C.F.R. 1.97(e)</li></ul> <p>AND</p> <ul style="list-style-type: none"><li><input type="checkbox"/> Applicants hereby requests consideration of the reference(s) disclosed herein. Please charge Deposit Account 19-1970 in the amount of \$180.00 under 37 C.F.R. 1.17(p). Please credit any overpayment or charge any underpayment to Deposit Account 19-1970. Election to pay the fee should not be taken as an indication that applicant(s) cannot execute a certification.</li></ul>

**Certification (37 C.F.R. 1.97(e))**  
(Applicable only if checked)

The undersigned certifies that:

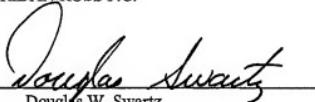
- Each item of information contained in this information disclosure statement was first cited in any communication from a foreign patent office in a counterpart foreign application not more than three months prior to the filing of this statement. 37 C.F.R. 1.97(e)(1).  
 A copy of the communication from the foreign patent office is enclosed.

OR

- No item of information contained in this information disclosure statement was cited in a communication from a foreign patent office in a counterpart foreign application, and, to the knowledge of the undersigned after making reasonable inquiry, no item of information contained in this Information Disclosure Statement was known to any individual designated in 37 C.F.R. 1.56(c) more than three months prior to the filing of this statement. 37 C.F.R. 1.97(e)(2).

Respectfully submitted,

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Date: Feb. 7, 2005

Substitute for form 1449A/PTO				<i>Complete if Known</i>	
<b>INFORMATION DISCLOSURE STATEMENT BY APPLICANT</b>				Application Number	10/614,340
				Filing Date	July 3, 2003
				First Named Inventor	ABRAMS, Louis Brown
				Art Unit	1733
				Examiner Name	
Sheet	1	of	1	Attorney Docket Number	4811-16

OTHER ART (Including Author, Title, Date, Pertinent Pages, etc.)		
Examiner Initials*	Cite No. <sup>1</sup>	

Examiner Signature		Date Considered	
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\*EXAMINER: Initial if reference is considered, whether or not citation is in conformance and not considered. Include copy of this form with next communication to applicant.



US006660352B2

(12) **United States Patent**  
Hsu et al.

(10) **Patent No.:** US 6,660,352 B2  
(45) **Date of Patent:** Dec. 9, 2003

(54)	<b>ADHESIVE ELECTROSTATIC SHEETS</b>		5,262,259 A	11/1993	Chou et al.
(75)	Inventors:	Chih-Chung Hsu, Woodbury, MN (US); Steven R. Austin, Oakdale, MN (US); Charles C. Lee, Little Canada, MN (US); Terry L. Morris, Eagan, MN (US)	5,264,291 A	1/1993	Shinozaki
			5,296,277 A	3/1994	Wilson et al.
			5,307,579 A	5/1994	Clayton et al.
			5,358,094 A	10/1994	Molinaro et al.
			5,409,181 A	4/1995	Lüthmann
			5,477,788 A	12/1995	Floegel
			5,488,455 A	1/1996	Cahill et al.
			5,507,464 A	4/1996	Hamerlik et al.
			5,516,588 A	5/1996	Kreckel et al.
			5,655,444 A	8/1997	Watanabe
			5,672,402 A	9/1997	Kreckel et al.
			5,702,803 A	12/1997	Eisele et al.
			5,766,394 A	6/1998	Cahill et al.
			5,795,425 A	8/1998	Brault et al.
			5,795,636 A	8/1998	Keller et al.
			5,807,624 A	9/1998	Anderson et al.
			5,837,375 A	11/1998	Brault et al.
			5,888,615 A	3/1999	Mascarenhas et al.
			5,904,984 A	5/1999	Ward et al.
			5,922,159 A	7/1999	Cahill
			5,965,235 A	10/1999	McGuire et al.
			5,989,685 A	11/1999	Hockaday
			6,001,471 A	12/1999	Bries et al.
			6,004,642 A	12/1999	Langford
			6,023,870 A	2/2000	McGarragh
			6,162,534 A	12/2000	Hamerlik
			6,258,200 B1 *	7/2001	Kassab ..... 156/273
			6,284,339 B1 *	9/2001	Floegel ..... 428/43
(21)	Appl. No.:	09/757,941			
(22)	Filed:	Jan. 9, 2001			
(65)	Prior Publication Data				
	US 2002/0090480 A1 Jul. 11, 2002				
(51)	Int. Cl. <sup>7</sup>	B32B 3/06; B32B 31/04			
(52)	U.S. Cl.	428/40.1; 40/593; 40/594; 40/611; 156/273.1; 156/267; 428/41.8; 428/42.1; 428/42.2; 428/203; 428/354			
(58)	Field of Search	428/40.1, 42.1, 428/42.2, 41.8, 203, 354; 156/273.1, 267; 40/593, 594, 611			
(56)	References Cited				
	U.S. PATENT DOCUMENTS				
3,301,741 A	1/1967	Henrikson et al.	DE	33 31 016	8/1983
3,314,838 A	4/1967	Erwin	EP	0 276 557 B1	4/1992
3,554,835 A	1/1971	Morgan	EP	0 279 579 B1	4/1993
3,924,561 A	12/1975	Rothart et al.	EP	0 371 635 B1	7/1996
3,967,022 A	6/1976	Hasei	GB	1 541 311	2/1979
4,023,570 A	5/1977	Chinai et al.	JP	56-80042	* 7/1981
4,024,312 A	5/1977	Korpman	WO	WO 85/04602	10/1985
4,054,697 A	10/1977	Reed et al.	WO	WO 90/0278	8/1990
4,151,319 A	4/1979	Sackoff et al.	WO	WO 91/06424	5/1991
4,226,910 A	10/1980	Dahlen et al.	WO	WO 92/00361	9/1992
4,362,591 A	12/1982	Tracy	WO	WO 95/06691	9/1995
4,376,151 A	3/1983	Parrotta	WO	WO 99/31193	6/1999
4,556,595 A	12/1985	Ochi	WO	WO 99/65999	12/1999
4,599,265 A	7/1988	Esmy			
4,735,837 A	4/1988	Miyasaka et al.			
4,862,944 A	9/1989	Hendershot			
5,008,139 A	4/1991	Ochi et al.			
5,010,671 A	4/1991	Stonehouse			
5,045,391 A	9/1991	Brant et al.			
5,106,710 A	4/1992	Wang et al.			
5,114,520 A	5/1992	Wang, Jr. et al.			
5,141,790 A	8/1992	Colhoun et al.			
5,162,138 A	* 11/1992	Colfisch .....	428/17		
5,207,581 A	5/1993	Beyd			
5,258,214 A	11/1993	Coolidge et al.			

## FOREIGN PATENT DOCUMENTS

DE	33 31 016	8/1983
EP	0 276 557 B1	4/1992
EP	0 279 579 B1	4/1993
EP	0 371 635 B1	7/1996
GB	1 541 311	2/1979
JP	56-80042	* 7/1981
WO	WO 85/04602	10/1985
WO	WO 90/0278	8/1990
WO	WO 91/06424	5/1991
WO	WO 92/00361	9/1992
WO	WO 95/06691	9/1995
WO	WO 99/31193	6/1999
WO	WO 99/65999	12/1999

\* cited by examiner

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## (57) ABSTRACT

Electrostatically charged graphic sheets are additionally provided with a preapplied activatable adhesive. Such sheets may be oriented on a display substrate using the electrostatically induced adhesion, and more securely fastened to the display substrate using the activatable adhesive.

1  
ADHESIVE ELECTROSTATIC SHEETS

## FIELD OF THE INVENTION

The present invention relates to sheets that electrostatically adhere to substrates. More specifically, the present invention relates to sheets that adhere to substrates using a combination of electrostatic charge and an additional adhesive.

## BACKGROUND OF THE INVENTION

Films have been provided with electrostatic charges, so that they will adhere to substrates without the use of adhesives. Films having persistent dielectric polarization are called electrets.

U.S. Pat. No. 5,258,214 discloses a preprinted thin plastic film wall covering having a preprinted image thereon and provided with a static electrical charge for securing the coverings to a surface.

U.S. Pat. No. 5,207,581 discloses a writing apparatus including electret film. The electret film, a flexible plastic film having a static electrical charge induced thereto, is capable of being erasably written upon with dry erase markers, as a writing medium. An apparatus is described for holding a roll of electret film.

U.S. Pat. No. 5,989,685 discloses an electret film composition adapted for printing on inkjet printers. This description provides an "improved printing material that incorporates the advantages of electrets (sic)" at column 2, lines 37-39. The advantages of electrets are stated at column 1, lines 53-55 to hold "the promise of providing a display which sticks to a surface without the use of fasteners or adhesives." The charged sheets of this invention are attached to a paper backing to avoid problems with handling of the sheets in the paper feed mechanisms of printers. These carrier backing papers are adhered to the sheets with a glued edge. Column 4, lines 24-52.

U.S. Pat. No. 5,807,624 discloses an electrostatically charged imaging manifold. The preferred imaging manifolds "comprise a transparent, polymeric sheet imageable in an imaging sheet, and attached thereto, an opaque member underlying and in register with said transparent sheet, said opaque member being adhered to said transparent polymeric sheet by means of the combination of an electrostatic charge and a pressure-sensitive adhesive." Column 3, lines 55-60. This adhesive is provided to provide additional protection against "scrunch," or to improve feeding performance of the sheet with the carrier paper. See column 12, line 66- column 13, line 2.

U.S. Pat. No. 6,023,870 describes an apparatus for displaying and replacing graphic sheet on vending machines, wherein graphics sheets are removably adhered to the reverse side of the clear display panel by static cling. An alternative embodiment is disclosed at column 7, lines 38-50, which describes the use of partial adhesive or reusable adhesive, defined as a "tacky" adhesive, for the removable adhering function. The adhesive described therein is the adhesive that is used on Post-it® brand notes from 3M, and particularly illustrating the tacky adhesive as SPRAY MOUNT® artist's adhesive from 3M, commercially available consumer applicable adhesive that can be applied on location. The specification further states that the principles of the various embodiments can be combined at Column 8, lines 32-36, giving the example that a tacky adhesive may secure the corners of a product graphics sheet that has been initially positioned using the method pertaining to static cling.

## 2

## SUMMARY OF THE INVENTION

The present invention provides a graphic sheet comprising a film having a top and bottom surface. The film has an electrostatic charge and additionally contains a preapplied activatable adhesive. The electrostatic charge is sufficient to support the sheet on a vertical clean insulated surface. The activatable adhesive is capable of assisting in adhesion of the sheet to a display substrate.

10  
DETAILED DESCRIPTION OF THE PRESENTLY PREFERRED EMBODIMENTS

As noted above, electrostatically charged sheets for application to various surfaces are known. The major advantage cited for these systems is the ability to adhere a sheet to an intended ultimate substrate without the use of adhesive. Thus, it was the primary objective in the prior art to avoid using an adhesive.

It has been found that over time that the charge in an electrostatically charged sheet will at least partially dissipate, and the adhesion of the sheet to the intended substrate will fail. This is particularly the case where sheets have been subjected to certain printing processes, such as offset printing. See U.S. Pat. No. 5,904,985 at column 2, lines 5-18. To provide adequate charge to hold the sheets at the desired location, the sheets have previously been recharged.

The present invention provides a combination adhesion system that provides adhesion both through electrostatic charge and also through a preapplied activatable adhesive. In the present invention, a positionable sheet is provided whereby the location of the sheet can be determined through the easily movable adhesion of the sheet to the display substrate, followed by more securely adhering the sheet to the substrate by the preapplied activatable adhesive. Prior uses of electrostatically charged sheet materials provided a graphic sheet that was subject to repositioning or even removal by accident. Thus, the accidental brush by a passerby or a gust of wind, such as from a fan, could move or remove the graphic sheet. The present invention provides secure adhesion for a graphics sheet that is attached to a display substrate using electrostatic charge.

In another aspect of the present invention, a more complete adhesion of the sheet to a display substrate is accomplished through the co-action of the electrostatic charge adhesion and the adhesion of the preapplied activatable adhesive. Thus, the entire sheet can be in intimate adhesive contact with the display substrate, even though conventional adhesive is located only at a few points. This provides the advantage of not having "tenting," or physical separation of the sheet from the display substrate, at portions of the sheet that does not have adhesive located thereon. Because there is co-action of both the electrostatic charge and the adhesive, the electrostatic charge does not have to be so strong as to support the entire weight of the graphic sheet over the entire life of the product. Likewise, the adhesive strength of the preapplied activatable adhesive need not be so strong as to support the entire weight of the graphic sheet over the entire life of the product, because it will be assisted by the adhesive effect of the electrostatic charge.

Additionally, the present invention makes it possible to achieve complete adhesion of the sheet to the display substrate without requiring a continuous coating of adhesive on the sheet. Sheets having a continuous coating of adhesive may be difficult to apply to a display substrate without creating wrinkles or capturing air bubbles. Thus, the present invention provides a graphic sheet that is easy for the

non-skilled person to apply to a display substrate and subsequently adjust to provide perfect positioning and appearance before commitment to that location by adhesion.

For purposes of the present invention, a "display substrate" is a substrate that is the desired ultimate location for placement of the sheet of the present invention for use in its final function as a graphic article, e.g. as a wallcovering or media surface. A display substrate is distinguished from a carrier substrate, in that a carrier is merely a vehicle for transporting a fragile film to another destination. Prior art films have used an adhesive for adhering a film to a carrier substrate, but this adhesive was then presumably destroyed or removed upon removal of the carrier substrate and before application of the electrostatic film to the display substrate. The prior art emphasizes the value of providing a sheet that adheres to the ultimate surface without resort to an adhesive. While the application of the sheet of the present invention to any particular display substrate may be temporary and subsequent applications of this sheet to another display substrate may be contemplated, the display substrate is not merely a carrier, and does not destroy the function of the adhesive before use of the sheet for its desired function.

For purposes of the present invention, a sheet is "securely" adhered to a substrate if, upon application of slight finger or hand pressure in a sliding action in a direction parallel to the surface of the display substrate, the sheet does not slide.

In a preferred embodiment of the present invention, the graphic sheet is imageable. In one preferred embodiment, the top surface of the film is imageable. In another preferred embodiment, the top surface of the film is coated to provide an imageable surface. In yet another preferred embodiment, the sheet is a laminate comprising an image receptive layer on the top surface of the film.

In an alternative embodiment of the present invention, the graphic sheet is a preimaged wallcovering. The present invention provides a significant benefit in this embodiment, in that an effective replacement for traditional wallpaper may now be provided. With the combination of adhesion through electrostatic charge and activatable adhesive, wall covering may now be applied without the use of messy liquid adhesives or pastes as conventionally used. Additionally, the present invention provides a substantially stable wallcovering, because there is no need to expose the hacking to water or other liquid during the application process that would expand the wallcovering when wet and shrink the wallcovering as it dries. The wallcovering may be applied to the wall with an infinite working time to position the covering to allow matching of patterns on the top surface of the graphic sheet and the like, with final adhesion only created when the applier is certain of proper placement. Thus, the preferred activatable adhesive is one that provides maximum positionability of the graphic sheet prior to final adhesion. Additionally, the activatable adhesive preferably creates a strong bond to the display substrate, so that the expected bonding lifetime for this preferred embodiment is at least 5 years or more.

Preferred embodiments of wallcovering according to the present invention are provided in a roll form that is at least 20 feet (6.1 meters) in one dimension. Particularly preferred embodiments of wallcovering have a pattern printed thereon having a matching design on one edge that, when mated to the corresponding pattern on the opposite edge of an adjacent sheet, provide an aesthetic overall design to the surface of the display substrate.

In another embodiment of the present invention, the graphic sheet is a writing surface capable of being written

upon after application to a display substrate. Preferably, the graphic sheet is capable of being erasably written upon, for example, with dry erase markers. In this embodiment, the sheet is an easily placeable writing surface that is a replacement or adjunct to the traditional blackboard writing surface.

The adhesive used in the graphic sheet of the present invention is a preapplied activatable adhesive. Thus, the graphic sheet construction is provided in a manner that is ready to apply to the intended display substrate without need for further assembly of parts at the location of the display substrate. This construction provides substantial advantages in time savings, simplicity of application and materials for the final applicator of the graphic sheet. The applicator of the graphic sheet of the present invention merely places the graphic sheet on the display substrate, positions the graphic sheet to its desired location and orientation, and activates the adhesive.

The activatable adhesive may be any appropriate adhesive system that has very low or no initial adhesion, but which can be activated to provide adhesive function as desired by the applicator. Examples of activatable adhesives include repositionable pressure sensitive adhesives, positionable pressure sensitive adhesives, pressure sensitive adhesives provided with a removable release liner, heat activated adhesives, microencapsulated adhesives, and the like.

In one embodiment of the present invention, the activatable adhesive is a repositionable pressure sensitive adhesive. As used herein, "repositionable" refers to the ability to be repeatedly adhered to and removed from a substrate without substantial loss of adhesion capability. Most preferably, the graphic sheet of the present invention may be adhered to and removed from a 20 pound white bond xerographic quality paper for 5 cycles using a 2 kg roller weight with no more than 75% loss of peel adhesion. In a preferred embodiment, the present invention is preferably removable from a display substrate when it has been adhered to the display substrate over a long period of time. Thus, preferably, the adhesive used in the present invention does not develop excessive adhesion build-up over time.

Preferably, the repositionable pressure sensitive adhesive provided on the film comprises between about 60-100% by weight of hollow, polymeric, acrylate, inherently tacky, infusible, solvent-insoluble, solvent-dispersible, elastomeric pressure-sensitive adhesive microspheres having a diameter of at least 1 micrometer, and between about 0-40% by weight of a non-spherical polyacrylate adhesive. These hollow microspheres are made in accordance with the teaching of European Patent Application 371,635. The non-spherical polyacrylate adhesive may be any conventional pressure-sensitive adhesive. Examples of such adhesives are polymers made from the "soft" monomers such as n-butyl acrylate, isoctyl acrylate, or the like, or copolymers made from a soft component, such as isobutylene, n-butyl acrylate, isoctyl acrylate, ethyl hexyl acrylate, or the like; and a polar monomer such as acrylic acid, acrylonitrile, acrylamide, methacrylic acid, methyl methacrylate or the like. Non-spherical polyacrylate adhesives are commercially available, for example, as the Rohm and Haas Rhoplex<sup>TM</sup> line of adhesives. Preferably, the non-spherical polyacrylate adhesive is present in the repositionable adhesive at an amount of about 10-35% by weight. When the repositionable adhesive additionally comprises a non-spherical polyacrylate adhesive, improved anchorage of the total adhesive to the sheet is observed, resulting in less adhesive residue being left on the substrate after removal. Also, tacky microsphere-containing repositionable adhesives comprising non-spherical polyacrylate adhesive exhibit excellent

shear adhesion properties, even for highly textured vertical surfaces. These advantageous adhesive properties are obtained without excessive adhesion to substrates such as painted walls that would result in peeling of the paint off of the wall when the film adhesive composite is removed.

Repositionable adhesives are also known in which microspheres contained in the adhesive are non-tacky. A disclosure of this type of adhesive is provided in U.S. Pat. No. 4,735,837 to Miyasaka.

A repositionable adhesive may be provided by addition of components to conventional adhesive formulations to modify their tack and flow characteristics. U.S. Pat. No. 4,599,265 (Esmay) discloses an adhesive having a high degree of cohesive strength that has low tack and maintains peelability from a variety of ordinary substrates. U.S. Pat. No. 4,737,559 (Kellen et al.) describes a PSA formulation in which the viscous flow, and resultant adhesion buildup, is controlled through the addition of a small amount of a free radically polymerizable photocrosslinker.

Another means for providing a repositionable adhesive through the reduction of the adhesive contact area is accomplished by the deposition of a discontinuous or patterned film on a backing. WO 85/04602 (Newing et al.) describes pressure-sensitive adhesive articles comprising a plurality of discontinuous adhesive segments in a pattern on at least a portion of at least one side of a carrier or backing, covering from about ten to about thirty percent of the total surface area of that carrier material. European Patent Application 276,557 (Fry) describes a repositionable pressure-sensitive sheet material comprising a sheet material bearing on one surface a discontinuous non-repository adhesive coating covering about 10 to about 85 percent of the surface in the form of individual adhesive islands. U.S. Pat. No. 4,889,234 (Sorenson et al.) discloses a discontinuous patterned adhesive label structure in which the level of adhesion is varied according to area of adhesive coverage on the label, the pattern in which the adhesive is coated, and the full coverage adhesive characteristics of the materials used. European Patent Application 279,579 (Tanuma et al.) describes pressure-sensitive adhesive sheets comprising, in one embodiment, a continuous adhesive layer having "irregular sections" (i.e., "... the pressure-sensitive adhesive layer is uneven . . ."). The uneven adhesive layer, according to the application, is imparted through a variety of pressing, molding, and embossing methods.

A preferred aspect of the present invention provides a sheet wherein the pressure sensitive adhesive is pattern coated on said bottom surface. The pattern coating preferably is provided in a striped pattern, so that some adhesive remains on the graphic sheet regardless of how the product may be trimmed by a printer or final user. In a preferred embodiment, the pressure sensitive adhesive covers less than 10% of the bottom surface of the film.

Most preferably, the activatable adhesive has virtually no initial adhesion, so that the graphic sheet may be easily slid after initial placement on the display substrate into final position.

In a particularly preferred embodiment of the present invention, the activatable adhesive is a positionable pressure sensitive adhesive. "Positionable" means a pressure sensitive adhesive that can be placed against a substrate surface and easily slid over the surface into proper position without preadhering or sticking the adhesive article in place using the activatable adhesive. Pressure subsequent to final placement of the graphic sheet is generally required to activate the adhesive. Alternatively, the adhesive may be engineered to build adhesion over time after placement on the display substrate.

In one embodiment, positionable adhesives may be provided by use of dry application aids, such as particles, Powders, or talcs have also proven useful in preventing preadhesion (See, e.g., U.S. Pat. Nos. 4,376,151 and 4,556,595). These techniques make application easy and provide for easy positioning and repositioning. These techniques may require contact of 1 to 7 days after activation to form a strong adhesive bond with the adhesive to the display substrate.

Alternatively, discontinuous coatings of nontacky materials that project from relatively planar adhesive surface may be used to prevent preadhesion of a pressure sensitive adhesive layer during application. These adhesive films and tapes have no adhesion when placed lightly against the substrate surface, and therefore can be placed against a substrate and freely moved over the substrate surface. Such coatings include patterned polymer coatings, particles, and films (See, e.g., U.S. Pat. Nos. 3,554,835; 4,023,570; 4,054,697; 4,151,319; 5,008,139; and U.K. Patent No. 1,541,311).

Another type of adhesive that is positionable comprises a random distribution of hollow glass microspheres partially embedded in an adhesive layer as a means to prevent contact and preadhesion (See U.S. Pat. No. 3,331,279). EG Tac™ brand adhesive films use similar "non-frangible" hollow glass microspheres partially embedded in the adhesive surface (See U.S. Pat. No. 5,008,139). Hi-S-Cal™ brand film with a "pressure-activated adhesive" that similarly used solid glass microspheres partially embedded in an adhesive surface as a means to prevent contact and preadhesion. In each case, application pressure to the sheet crushes and/or embeds the microspheres into the adhesive layer permitting the bulk of the adhesive to contact the substrate and to instantly form a strong bond.

Alternatively, U.S. Pat. No. 3,314,838 describes a similar configuration wherein the tops of the hollow microspheres protruding from the adhesive layer surface are coated by a thin layer of pressure sensitive adhesive. Application of pressure crushes the microspheres, permitting the bulk of the adhesive layer to contact the substrate and to form a strong bond.

Other methods for handling preadhesion include formation of brittle plastic projections on a PSA surface (See U.S. Pat. No. 3,301,741), or formation of small discrete clusters of particles protruding from the adhesive surface (See U.S. Pat. No. 5,141,790). For example in U.S. Pat. No. 5,141,790, the particles were tacky adhesive microspheres that provided weak bonding to a substrate when applied using light application pressure and strong bonding when applied using higher application pressures.

Topologically structured adhesives may also be used to provide a positionable adhesive. For example, relatively large scale embossing of an adhesive has been described to permanently reduce the pressure sensitive adhesive/substrate contact area and hence the bonding strength of the pressure sensitive adhesive (See EPO 0 279 579). Various topologies include concave and convex V-grooves, diamonds, cups, hemispheres, cones, volcanoes and other three dimensional shapes all having top surface areas significantly smaller than the base surface of the adhesive layer. In general, these topologies provide adhesive sheets, films and tapes with lower peel adhesion values in comparison with smooth surfaced adhesive layers. In many cases, the topologically structured surface adhesives also display a slow build in adhesion with increasing contact time.

An adhesive sheet having a microstructured adhesive surface comprising a uniform distribution of adhesive or

composite adhesive "pegs" over the functional portion of an adhesive surface and protruding outwardly from the adhesive surface provide a sheet that is both positionable and repositionable when it is laid on a substrate surface (See U.S. Pat. No. 5,296,277). Pressing the adhesive sheet results in an instant formation of a strong bond between the adhesive sheet and the substrate. Such an adhesive also required a relatively expensive coincident microstructured release liner to protect the adhesive pegs during storage and processing.

A positionable-repositionable pressure sensitive adhesive is described in WO 91/06424. This adhesive contains a mixture of adhesive resin, detackifying resin, detackifying particles and tackifying resin. Sheet articles having a layer of this adhesive exhibit low tack, for easy positioning, and a low initial bond when pressed in place, for easy repositioning. Adhesive films having this kind of adhesive exhibit the ability to slide over a surface on contact, and bond with modest strength when pressed in place. The adhesive coated films slide freely when removed and recontacted to the surface. However, this adhesive shows only slow adhesion build. This slow adhesion build can increase installation time, such as when a large graphic is applied to a truck siding, the adhesion must be sufficient to allow the operation of the vehicle at normal operating speeds. Furthermore, the adhesive film sticks over a very limited application temperature range.

A particularly preferred positionable adhesive is described in U.S. Pat. No. 5,795,636, which provides an adhesive layer that (1) has microstructural surface features that impart positionable and repositionable behavior to the adhesive sheet, and (2) is sufficiently elastic to permit these microstructural surface features to rapidly recover the major portion of their size and shape when the applied article is removed from a substrate, backing, or release liner surface.

In yet another embodiment, the bottom surface of the graphic sheet may be provided with a non-uniform surface topography, with protrusions of the graphic sheet bottom surface being in initial contact with the display substrate and with valleys or depressions between the protrusions of the graphic sheet bottom surface being coated with an adhesive. Upon placement of the graphic sheet on the display substrate, additional pressure to the graphic sheet compresses the protrusions and allows the adhesive located in the depressions to contact the display substrate, thereby adhesively adhering the graphic sheet to the display substrate. One such construction containing random protrusions is described in U.S. Pat. No. 5,965,235. Alternatively, the protrusions can be regularly oriented in the form of ridges or other such geometry, with the depressions being oriented as regular channels or grooves.

Alternatively, the activatable adhesive is activated by introduction of energy, such as heat or radiation (including microwave, UV light, visible light, or the like). A particularly preferred embodiment comprises the use of heat activated adhesive, which is essentially the provision of a hot melt adhesive on the bottom surface of the graphic sheet. Preferably, the heat activated adhesive may be activated by application of heat from a hand-held heating device similar to a hair dryer.

In another alternative embodiment of the present invention, the activatable adhesive is microencapsulated. In this embodiment, the adhesive remains within the microcapsules until release. The sheet therefore can be applied to the display substrate, and the additional adhesion provided by the pressure sensitive adhesive is not activated until the triggered release of the microcapsules. The microcapsules

may release the pressure sensitive adhesive in any manner, but most conventionally the microcapsules will release the adhesive upon rupture. In a preferred application method, the sheet is applied to the display substrate and positioned while being lightly adhered by the electrostatic charge. Upon proper placement on the display substrate, the applicator applies additional pressure to the sheet in the location of the capsules, thereby rupturing the capsules and releasing the adhesive.

10 Adhesives may be microencapsulated by any appropriate technique in the art, such as interfacial encapsulation, complex coacervation, and the like. The adhesives to be encapsulated may be pressure sensitive adhesives, or may be adhesives that cure upon release from the microcapsule, either by exposure to the air or by reaction with another reactant either on the surface of the film or display substrate, or separately encapsulated.

In a yet another embodiment, the activatable adhesive is a pressure sensitive adhesive that is protected from premature adhesion by a release liner, and the adhesive so protected is activated by removal of the release liner. Most preferably, this embodiment utilizes a stretch release configuration to provide a construction that is easily removable without damaging the display substrate or, most preferably, the graphic sheet.

The use of the stretch release adhesive tape allows for an adhesive system to be used that will adhere to any surface, yet be cleanly removable without causing damage to that surface. Thus even very aggressive adhesives can be used in the stretch release tape such that the graphic sheet can be made to adhere to difficult rough surfaces, such as painted brick, without falling off of the display substrate. Even with the aggressive adhesive, the product can be safely removed without damage to the display substrate (e.g., removing the paint on a painted surface) due to the stretch release configuration of the pressure sensitive adhesive.

When the activatable adhesive is a stretch release configuration, it is provided as a double-sided pressure sensitive adhesive ("DSPSA") wherein pressure sensitive adhesive is provided on both sides of an extensible backing. Such adhesive articles may be generically referred to as a stretch release adhesive tape. These tapes operate in that when the backing is stretched after the tape is adhered on one side or both sides, the adhesive stretches and undergoes clean interfacial debonding from the substrate or substrates to which it is adhered. Such removal typically progresses from one end of the tape to the other as the tape backing is stretched at an angle preferably no greater than about 35° from the surface of the substrate. That is, as the tape is stretched from one end, it debonds from the end being stretched toward its distal end.

Particularly preferred embodiments of the stretch release configuration use adhesive tapes that have plastic backings. That means, as the backing is stretched, it is permanently deformed and has relatively low elastic recovery. Such tapes include tapes comprising film layers, foam layers, and laminates of films and/or foams.

Co-pending U.S. patent application Ser. No. 08/308,937 (WO 95/06691), which is commonly owned by the Assignee of the present invention, discloses a number of stretchable release tapes comprising constructions of films, foams, and laminates of films and/or foams. Again, such tapes include conventional pressure-sensitive adhesives.

65 Another type of stretchable release adhesive tape is described in U.S. Pat. No. 5,409,189 to Lühmann, wherein the adhesive tape backings utilized comprise elastic mate-

rials. Elastic, as opposed to plastic materials described above, means materials that are stretchable without substantial plastic deformation and which have high elastic recovery after stretching and release. Like the plastic tapes described above, elastic tapes can be single-sided or double-sided and the stretching of the backing causes adhesive stretching and subsequent debonding of the adhesive surface or surfaces from the stretched end to the distal end as the tape is stretched.

Preferred embodiments of stretchable release tapes that may be used in the present invention are described in U.S. Pat. No. 6,001,471. Other preferred embodiments are described in U.S. Pat. Nos. 5,672,402; 5,516,581; 4,024,312; 6,162,534; and German Pat. Document 33 31 016C2. In addition, the stretch releasing tape can include a splitable layer such as the layers described in U.S. Pat. No. 6,004,642, or a re-fastenable layer such as the layers described in PCT International Publication No. WO 99/31931 (U.S. patent application Ser. No. 08/989,507, filed Dec. 12, 1997).

Commercial stretch releasing adhesive tapes include the product sold under the trade designation COMMAND by Minnesota Mining and Manufacturing Company, St. Paul, Minn., and the product sold under the trade designation POWER-STRIPS by Beiersdorf AG, Hamburg, Germany. These products are currently manufactured as discrete strips with one end of the strip including a non-adhesive pull tab to facilitate stretching of the strip during removal. The adhesive surfaces of the strip are additionally protected with a release liner.

Optionally, the side of the DSPSA that is to be applied to the graphic sheet may be selected from any pressure sensitive adhesive. Preferably, the side of the DSPSA that is to be applied to the graphic sheet is also easily removed from the graphic sheet without damage to said sheet. By "removable" is meant that the adhesive can be removed from the substrate without damage to that substrate. Preferably, the adhesive can be removed from a sheet of U.S. Gypsum  $\frac{3}{8}$ " (9.5 mm) sheetrock that was painted first with Sherwin Williams ProMar<sup>TM</sup> 200 interior latex primer, then with a single top coat of Sherwin Williams Classic<sup>TM</sup> 99 interior flat latex wall paint. The painted wallboard was aged under ambient conditions at about 22° C. for a minimum of 48 hours prior to use for testing. More preferably, said adhesive can be removed from 20 pound white bond xerographic quality paper without tearing the paper.

In a preferred embodiment of the present invention, the display substrate side of the DSPSA is a repositionable pressure sensitive adhesive as defined above.

The graphic sheet of the present invention may be provided in any shape. Preferably, the graphic sheet is rectangular or square, and the activatable adhesive is located at the corners of the film.

An electrostatically charged film is prepared by passing the film through an electrostatic field. This field can be generated by any known electric charge generator, e.g., a corona charger, a tribocharger, conducting high potential roll charge generator or contact charger, static charge generator, and the like. Samples may be charged with a DC charge or a DC charge followed by an AC charge in order to create an adequate level of charge adhesion between the two surfaces. Preferably, the film is passed through the electrostatic field while in a molten or semi-molten state, and is cooled down before the charge dissipates, thereby "locking in" the charge and providing an electret having long-lasting electrostatic properties. The film is sufficiently charged so as to be able to support the graphic sheet on a vertical clean

insulated surface. The ability of a graphic sheet to so support itself is evaluated by application to a sheet of U.S. Gypsum  $\frac{3}{8}$ " (9.5 mm) sheetrock that was painted first with Sherwin Williams ProMar<sup>TM</sup> 200 interior latex primer, then with a single top coat of Sherwin Williams Classic<sup>TM</sup> 99 interior flat latex wall paint. The painted wallboard was aged under ambient conditions at about 22° C. for a minimum of 48 hours prior to use for testing. A graphic sheet is considered to be able to support itself if, upon placement on a vertical surface as described above without activation of the activatable adhesive at a temperature of about 22° C., the sheet does not fall off for at least five minutes.

Preferably, the film comprises a polymer selected from the group consisting of polypropylene, polyethylene, polyester, polyamide, polyimide, polyurethane, polyethylene acrylic acid, polyvinyl chloride, polyethylene methacrylic acid, thermoplastic rubbers, polypropylene oxides, polystyrenes, polystyrene-polydiene block copolymers, ionic thermoplastic elastomers, polyethers, polyesteramides, polyetherestersamides, siloxanes, ethylene vinyl acetate, polymethyl methacrylate (PMMA), polyvinyl dichloride (PVDC), acetate copolymers, polybutenes, fluorine-containing elastomers, silicone rubbers, polycaprolactones, and elastomeric block copolymers, and blends and combinations thereof.

In a particularly preferred embodiment, the graphic sheet of the present invention is imageable. In one embodiment, the electrostatically charged film is selected from a film chemistry that is receptive to receive and retain the printing of an image thereon. Alternatively, the electrostatically charged film is treated physically or chemically using techniques well known in the art to enhance the image reception and retention of the film chemistry. In another embodiment, the graphic sheet is provided as a laminate, with an image receptive layer laminated to the film. Lamination may be by any appropriate technique in the art, such as by adhesion or coextrusion. The film may be electrostatically charged either before or after treatment or lamination to provide the image receptive graphic sheet.

Preferably, the imageable graphic sheet is receptive to one or more of a wide variety of imaging methods, such as electrophotography, screen printing, thermal mass transfer, ink jet (including ink jet techniques using water soluble inks, solvent based inks or UV curable inks), flexography, dye sublimation, or other printing processes.

In addition to the optional layers mentioned above, a multilayer sheet in accordance with the present invention can include other optional layers, such as an abrasion and/or graffiti resistant layer and the like.

Optionally, the bottom surface of the graphic sheet may be provided with a surface topography such that fluid (including air) is allowed to escape as the bottom surface of the graphic sheet is applied to the display substrate. Preferably, the topography of the bottom surface is such that a person of ordinary vision cannot detect the presence of entrapped air bubbles at a distance of two meters from the graphic sheet after application to a display substrate. Preferably, this topography is provided in the form of microchannels or grooves provided in a pattern effective to reduce or eliminate formation of visible entrapped air bubbles between the graphic sheet and the display substrate. The preferred microchannels may have any appropriate cross-sectional shape, such as round, square, triangular or trapezoidal. Size of the microchannels may depend on the thickness of the graphic sheet, and preferably may be in the range of less than 0.1 mm wide and less than 25 mm deep.

Preferably, the microchannels are arrayed such that the electrostatic cling performance of the graphic sheet is not adversely affected. Most preferably, the bottom surface of the graphic sheet has a contact area to the display substrate of at least 35%. Additionally, the topography of the bottom surface of the graphic sheet is preferably designed such its presence does not adversely effect the appearance of the graphic after application to the display substrate. Most preferably, the topography of the bottom surface is such that a person of ordinary vision cannot detect its presence at a distance of two meters from the graphic sheet after application to a display substrate. Examples of such topography are described in U.S. patent application Ser. No. 09/098,961, filed Jun. 18, 1998 (WO 99/65399).

Any of the layers above, whether optional or not, may include at least one optional additive. An optional additive can be selected from additional pigments, colorants, fillers, ultraviolet (UV) absorbing agents, antiblocking agents, flame retardant agents, plasticizers, light stabilizers, heat stabilizers, slip agents, antistatic agents, free radical scavengers, and carrier resins for such additives, all of which are familiar to those skilled in the art. These additives are preferably chosen so as not to interfere with a coextrusion processes, image receptivity, structural integrity any layer or the combination of any multilayer embodiment, and the like.

The present invention also provides a method of applying a graphic sheet to a display substrate, comprising:

applying the bottom surface of the film to the intended location on the display substrate, thereby temporarily adhering the sheet to the display substrate through the electrostatic charge of the film;  
orienting said sheet on the display substrate; and  
securely adhering the sheet to the display substrate by activation of the activatable adhesive.

In a preferred embodiment of this method, the activatable adhesive is a pressure sensitive adhesive that has been protected from premature adhesion by a release liner, and the release liner is removed after orienting the sheet on the display substrate.

In another preferred embodiment of this method, the activatable adhesive is microencapsulated, and the adhesive is released from said microcapsules after orienting the sheet on the display substrate.

In another preferred embodiment of this method, the activatable adhesive is a positionable pressure sensitive adhesive that is activated by pressure, and wherein the adhesive is activated by applying pressure to the sheet at the location of the adhesive after orienting the sheet on the display substrate.

In another preferred embodiment of this method, the activatable adhesive is a repositionable pressure sensitive adhesive, and wherein the adhesive is activated by applying additional pressure to the sheet adhesive at the location of the adhesive to assure good contact of the adhesive to the display substrate after orienting the sheet on the display substrate.

In another preferred embodiment of this method, the activatable adhesive is a pressure sensitive stretch adhesive that has been protected from premature adhesion by a release liner, wherein the adhesive is activated by removal of the release liner after orienting the sheet on the display substrate, wherein the method further comprises the step of removing the sheet from the display substrate, comprising stretching the backing of the stretch adhesive at an angle no greater than about 35° from the surface of the display substrate, thereby removing the adhesive without damage to the display substrate.

The disclosures of patents and patent applications cited herein are hereby incorporated by reference.

What is claimed is:

1. A graphic sheet comprising a film having a top and bottom surface, said film having an electrostatic charge, said bottom surface further comprising a preapplied activatable adhesive, said electrostatic charge being sufficient to support said sheet on a vertical clean insulated surface and said activatable adhesive having an exposed surface.
2. The graphic sheet of claim 1, wherein the activatable adhesive is pattern coated on said bottom surface of the film.
3. The graphic sheet of claim 2, wherein the activatable adhesive covers less than 10% of the bottom surface of the film.
4. The graphic sheet of claim 1, wherein the activatable adhesive is microencapsulated.
5. The graphic sheet of claim 1, wherein the sheet is rectangular or square, and the activatable adhesive is located at the corners of the film.
6. The graphic sheet of claim 1, wherein the sheet is imageable.
7. The graphic sheet of claim 1, wherein the top surface of the film is imageable.
8. The graphic sheet of claim 1, wherein the sheet is a laminate comprising an image receptive layer on the top surface of the film.
9. The graphic sheet of claim 1, wherein the sheet is a preimaged wallcovering.
10. The graphic sheet of claim 9, wherein said wallcovering is provided in a roll form that is at least 20 feet in one dimension.
11. The graphic sheet of claim 1, wherein the graphic sheet is a writing surface capable of being written upon after placement on a display substrate.
12. The graphic sheet of claim 1, wherein the graphic sheet is a writing surface capable of being written upon with dry erase markers after placement on a display substrate.
13. The graphic sheet of claim 1, wherein the bottom surface of the graphic sheet is provided with a surface topography such that fluid is allowed to escape as the bottom surface of the graphic sheet is applied to the display substrate.
14. A graphic sheet comprising a film having a top and bottom surface, said film having an electrostatic charge, said bottom surface of said film further comprising a preapplied pressure sensitive adhesive with a removable release liner, said electrostatic charge being sufficient to support said sheet on a vertical clean insulated surface.
15. The graphic sheet of claim 14, wherein the activatable adhesive is a pressure sensitive repositionable adhesive.
16. The graphic sheet of claim 15, wherein the pressure sensitive adhesive comprises inherently tacky microspheres.
17. The graphic sheet of claim 14, wherein the activatable adhesive is a pressure sensitive positionable adhesive.
18. The graphic sheet of claim 17, wherein the pressure sensitive adhesive comprises nonsticky projections from a pressure sensitive adhesive surface.
19. The graphic sheet of claim 14, wherein the activatable adhesive is a pressure sensitive adhesive provided on both sides of an extensible hacking.
20. A graphic sheet comprising a film having a top and bottom surface, said film having an electrostatic charge sufficient to support said sheet on a vertical clean insulated surface, said bottom surface of said film further comprising preapplied activatable adhesive.
21. A method of applying a graphic sheet of claim 20 to a display substrate, comprising:

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- a) applying the bottom surface of the film to the intended location on the display substrate, thereby temporarily adhering the sheet to the display substrate through the electrostatic charge of the film;
- b) orienting said sheet on the display substrate; and
- c) securely adhering the sheet to the display substrate by activating the activatable adhesive.

22. The method of claim 21, wherein the activatable adhesive is microencapsulated, and wherein the adhesive is released from said microcapsules after orienting the sheet on the display substrate.

23. The method of claim 21, wherein the activatable adhesive is a positionable pressure sensitive adhesive that is activated by pressure, and wherein the adhesive is activated by applying pressure to the sheet at the location of the adhesive after orienting the sheet on the display substrate.

24. The method of claim 21, wherein the activatable adhesive is a repositionable pressure sensitive adhesive, and wherein additional pressure is applied to the adhesive at the location of the adhesive to assure good contact of the adhesive to the display substrate after orienting the sheet on the display substrate.

25. A method of applying a graphic sheet to a display substrate, comprising:

- a) providing a graphic sheet comprising a film having a top and bottom surface, said film having an electro-

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static charge, said bottom surface of said film further comprising a preapplied pressure sensitive adhesive with a removable release liner, said electrostatic charge being sufficient to support said sheet on a vertical clean insulated surface;

b) applying the bottom surface of the film to the intended location on the display substrate, thereby temporarily adhering the sheet to the display substrate through the electrostatic charge of the film;

- c) orienting said sheet on the display substrate;
- d) removing the release liner from the pressure sensitive adhesive, thereby exposing said adhesive; and
- e) applying said exposed adhesive to the display substrate, thereby securely adhering the sheet to the display substrate.

26. The method of claim 25, wherein the pressure sensitive adhesive is a stretch adhesive comprising an extensible backing; wherein the method further comprises the step of removing the sheet from the display substrate, comprising stretching the backing of the stretch adhesive at an angle no greater than about 35° from the surface of the display substrate, thereby removing the stretch adhesive without damage to the display substrate.

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Keep et al.

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(54) **STABILIZED POLYESTER FIBERS AND FILMS**

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(58) Field of Search 528/295, 298, 528/302, 306, 307, 308, 308.6; 525/438; 524/126; 524/128; 428/359, 364, 373

(56) **References Cited**

## U.S. PATENT DOCUMENTS

3,051,212 A	8/1962 Daniels
3,193,522 A	7/1965 Neumann et al.
3,193,523 A	7/1965 Neumann et al.
3,560,605 A	2/1971 Sigel et al.
3,589,956 A	6/1971 Kranz et al.
3,627,867 A	12/1971 Schwarz
3,657,191 A	4/1972 Titzmann et al.
3,672,144 A	6/1972 Weisermel et al.
3,869,427 A	3/1975 Meschke et al.
3,975,329 A	8/1976 Barnewell et al.
4,016,442 A	4/1977 Alexander et al.
4,115,350 A	9/1978 Lazarus et al.
4,130,541 A	12/1978 Lazarus et al.
4,130,601 A	12/1978 Ohoka et al.
4,139,521 A	2/1979 Lazarus et al.
4,222,928 A	9/1980 Kawamura et al.
4,308,195 A	12/1981 Mayer et al.

4,310,658 A	1/1982 Lazarus et al.
4,348,500 A	9/1982 Robeson et al.
4,374,961 A	2/1983 Rothwell et al.
4,529,779 A	7/1983 Arai et al.
4,879,328 A	11/1989 Karasawa et al.
5,169,499 A	12/1992 Eagles et al.
5,428,086 A	6/1995 Minnick et al.
5,596,049 A	* 1/1997 Gallucci et al. .... 525/438
5,607,757 A	3/1997 Dalton
5,981,062 A	11/1999 Stroud, Jr. et al.
6,132,868 A	10/2000 Dean et al.

## FOREIGN PATENT DOCUMENTS

CH	601 391	12/1977
EP	0 273 149 A2	6/1988
GB	1 601 585	11/1981
JP	54-04258	4/1979
JP	54-131695	10/1979
JP	55-12871	1/1980
JP	57-161124	10/1982
JP	59-163479	9/1984
JP	61-36009	8/1986
JP	7-166419	6/1995
JP	8-208965	8/1996
JP	2002-69777	3/2002
JP	2002-115121	4/2002

\* cited by examiner

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(57) **ABSTRACT**

Disclosed are fibers and films prepared from polyesters of a dicarboxylic acid, preferably terephthalic acid, and a diol selected from 1,3-cyclohexanedimethanol, or 1,3-propanediol. The fibers and films contain a multifunctional epoxide additive and, optionally, an antioxidant, and show an increased dry heat stability when exposed to elevated temperatures in the presence of air while preserving excellent hydrolytic stability. Also disclosed is a process for stabilizing polyester fibers by melt blending a polyester and epoxide additive and melt spinning. The fibers and films are particularly useful in applications requiring elevated temperatures.

31 Claims, No Drawings

## STABILIZED POLYESTER FIBERS AND FILMS

## FIELD OF THE INVENTION

The present invention pertains to fibers and films prepared from polyesters of a dicarboxylic acid and a diol selected from 1,3-cyclohexanedimethanol, 1,4-cyclohexanedimethanol, or 1,3-propanediol. The fibers and films contain an epoxide additive and, optionally, an antioxidant, and show an increased dry heat stability when exposed to elevated temperatures in the presence of air. The fibers and films are particularly useful in applications requiring elevated temperatures.

## BACKGROUND OF THE INVENTION

Polyester materials are widely used as extrusion and molding resins for applications such as fibers, films, automotive parts, food packaging, beverage containers, and the like. Commonly used polyesters include poly(ethylene terephthalate), herein abbreviated as "PET", poly(1,4-butyleneterephthalate), herein abbreviated as "PBT", poly(1,3-propylene terephthalate), herein abbreviated as "PTT", and poly(1,4-cyclohexylenedimethylene terephthalate), herein abbreviated as "PCT". PET polymers are widely used because of their availability and modest price. PET polymers have relatively good heat resistance in dry conditions but tend to degrade readily under moist conditions at elevated temperatures. Similarly, PET fibers, yarns, and fabrics are known to exhibit excellent dimensional stability, that is, low shrinkage or growth during service. Although PET has a high resistance to thermal degradation, PET fibers can exhibit loss of tensile strength under continuous exposure to elevated temperatures. Because of these limitations, PET polymers have limited usefulness in certain durable and semi-durable applications which require elevated temperatures, such as, for example, paper making machine clothing, dryer belts, industrial belts, high temperature tape backing, filter media for air or liquid filtration, autoclave products, and other applications involving extended exposure to steam or superheated steam.

Efforts to remedy this problem have been directed to producing a high molecular weight linear polyester having a low content of free carboxyl groups. One approach is to reduce the number of free carboxyls by the use of "end-capping agents", such as diazomethane, as disclosed by U.S. Pat. No. 3,051,212, or carbodiimides, as disclosed by U.S. Pat. Nos. 3,975,329 and 5,169,499, which react with the free carboxyl groups and thereby prevent their further reaction. These end-capping materials, however, are expensive, often toxic, and thus not suitable for commercial applications.

Polyester compositions containing epoxides are known (see, for example, U.S. Pat. Nos. 3,657,191; 3,627,867; 3,869,427; 4,016,142; 4,130,541; 4,115,350; 3,560,605; 55 4,374,960; and Japanese Kokai Patent Nos. 07166419; 55012871; and 54131695). The addition of epoxides to polyesters, however, can be problematic. For example, the epoxides may show a low reactivity which, in turn, can create processing and operational difficulties and give uncertain results. For example, U.S. Pat. No. 3,869,427 discloses that styrene oxide appears to increase the level of carboxyl groups when added to molten PET and that diepoxides are "unsuitable for the formation of fibers". Various polyester blends and composites in combination with epoxides also are described, for example in U.S. Pat. Nos. 4,348,500 and 4,222,928. Such blends, however, are expensive and can

require complicated processing. In addition, reinforced polymer composites are not suitable for the preparation of fibers. Thus the compositions described in the above references do not adequately address the inherent susceptibility of PET to hydrolysis or provide compositions which show excellent stability to high temperatures under both dry and moist conditions.

In contrast to PET, polyester polymers based on poly(1,4-cyclohexylenedimethylene terephthalate), i.e., "PCT", have excellent high temperature hydrolytic stability, are essentially free of cyclic trimers and surface oligomers, and are well suited for filtration applications. PCT fibers have an inherent advantages, with melting points (abbreviated herein as "T<sub>m</sub>") up to 290° C., glass transition temperatures (abbreviated herein as "T<sub>g</sub>") up to 90° C., high resiliency, and softness in comparison with other polyester fibers. PCT polymers, however, are susceptible to oxidation and tend to degrade when heated at high temperatures in the presence of air. Although PCT polymers containing epoxides and antioxidants for molding and reinforced compositions also are known (see, for example, Minnick et al. in U.S. Pat. No. 5,428,086), the deficiencies of PCT polymers in dry-heat stability for fiber and film applications have not been addressed. We have now discovered that fibers and films prepared from PCT and PTT homo- and copolymers melt-blended with multifunctional epoxides show excellent stability at elevated temperatures in the presence of air and under both moist and dry conditions. Our discovery is unexpected because fibers and films prepared from PET melt-blended with multifunctional epoxides show no improvement, and sometimes, a reduction in both dry and wet stability at elevated temperatures.

## SUMMARY OF THE INVENTION

It has been found that certain polyester blends containing selected epoxide compounds and, optionally, antioxidants, such as hindered phenols and/or phosphites, have excellent elevated temperature stability in fiber and film form under both dry and moist conditions. Accordingly the present invention provides a polyester fiber comprising:

- i) dicarboxylic acid residues comprising about 60 to 100 mole % of a first dicarboxylic acid residue selected from the group consisting of terephthalic acid, naphthalenedicarboxylic acids, cyclohexanedicarboxylic acids, and mixtures thereof; and from 0 to about 40% of a second dicarboxylic acid residue selected from the group consisting of aromatic dicarboxylic acids containing from about 8 to about 16 carbon atoms, aliphatic dicarboxylic acids containing from about 4 to about 16 carbon atoms, cycloaliphatic dicarboxylic acids containing from about 6 to about 16 carbon atoms, and mixtures thereof;
- ii) diol residues comprising about 50 to 100 mole % of a first diol residue selected from the group consisting of 1,3-cyclohexanedimethanol, 1,4-cyclohexanedimethanol, 1,3-propanediol, and mixtures thereof, and from 0 to about 50 mole % of a second diol residue selected from the group consisting of aliphatic diols containing from 2 to about 16 carbon atoms, cycloaliphatic diols containing from about 6 to about 16 carbon atoms, and mixtures thereof;
- iii) about 0.05 weight % (wt %) to about 15 wt %, based on the total weight of said polyester, of an epoxide additive comprising an epoxide compound with at least 2 epoxy groups per molecule.

The fiber compositions may take any of the following forms, namely monofilaments, multifilaments, tows, staple

or cut fibers, staple yarns, cords, woven, tufted and knitted fabrics, nonwoven fabrics, including melt blown fabrics and spunbond fabrics, and multilayer nonwovens, laminates, and composites from such fibers. Because of their good resistance to degradation at elevated temperatures, our novel stabilized fibers are useful in dryer felts and other paper machine clothing, belting, filter media for hot air or hot liquid filtration, electrical, autoclavable, sterilizable products, and other industrial applications.

The instant invention also provides stabilized polyester films. Thus, another embodiment of our invention is polyester film comprising:

- a polyester comprising about 60 to 100 mole % of a dicarboxylic acid residue selected from the group consisting of terephthalic acid, naphthalenedicarboxylic acids, cyclohexanedicarboxylic acids, and mixtures thereof; about 50 to 100 mole % of a diol residue selected from the group consisting of 1,3-cyclohexanediethanol, 1,4-cyclohexanediethanol, 1,3-propanediol, and mixtures thereof; and
- about 0.05 weight % (wt %) to about 5 wt %, based on the total weight of said polyester, of an epoxide additive comprising an epoxide compound with at least 2 epoxy groups per molecule.

These films are useful for food, industrial, and medical packaging used under high temperature conditions, including membranes and supports for biculture media.

Our invention also provides a process for stabilizing polyester fibers comprising:

- melt blending a) a polyester comprising about 60 to 100 mole % of a dicarboxylic acid residue selected from the group consisting of terephthalic acid, naphthalenedicarboxylic acids, cyclohexanedicarboxylic acids, and mixtures thereof; about 50 to 100 mole % of a diol residue selected from the group consisting of 1,3-cyclohexanediethanol, 1,4-cyclohexanediethanol, 1,3-propanediol, and mixtures thereof; b) about 0.05 wt % to about 5 wt %, based on the total weight of said polyester, of an epoxide additive comprising a epoxide compound with at least 2 epoxy groups per molecule; and
- melt spinning continuous strands of filaments.

The present invention thus provides polyester fibers and films with increased stability at elevated temperatures under both moist and dry conditions and in the presence of air. Our novel fibers and films may contain from 0 weight % to about 6 weight % (abbreviated hereinafter as "wt %"), based on the total weight of the polyester, of a hindered phenol, phosphorus-containing, or sulfur-containing antioxidant to provide additional stability. Our invention may be used to prepare a range of fiber types including monofilament, multifilament, yarns, bicomponent fibers, spunbond fabrics, and melt blown webs. The fibers may be readily produced in a range of sizes from about 2 micrometers (also referred to herein as "microns" and abbreviated as " $\mu\text{m}$ ") in melt blown webs, about 0.5 to about 50 d/f for staple fibers, and up to about 5000 d/f for monofilament. The fibers of our invention may also be used in crimped and uncrimped form. Our novel fibers and films thus solve many of the known dry heat and hydrolytic stability problems encountered with PET and other polyester materials and provide longer lived, more economical products.

#### DETAILED DESCRIPTION

The present invention provides polyester fiber and films which show increased dry heat and hydrolytic stability in the presence of air at elevated temperatures. In a general embodiment, our invention provides polyester fiber and

films comprising i) dicarboxylic acid residues comprising about 60 to 100 mole % of a first dicarboxylic acid residue selected from the group consisting of terephthalic acid, naphthalenedicarboxylic acids, cyclohexanedicarboxylic acids, and mixtures thereof; a second dicarboxylic acid residue from 0 to about 40% of a second dicarboxylic acid residue selected from the group consisting of aromatic dicarboxylic acids containing from about 8 to about 16 carbon atoms, aliphatic dicarboxylic acids containing from about 4 to about 16 carbon atoms, cycloaliphatic dicarboxylic acids containing from about 6 to about 16 carbon atoms, and mixtures thereof; ii) diol residues comprising from about 50 to 100 mole % of a first diol residue selected from the group consisting of 1,3-cyclohexanediethanol, 1,4-cyclohexanediethanol, 1,3-propanediol, and mixtures thereof; from 0 to about 50 mole % of a second diol residue selected from the group consisting of aliphatic diols containing from 2 to about 16 carbon atoms, cycloaliphatic diols containing from about 6 to about 16 carbon atoms, and mixtures thereof; and iii) about 0.05 weight % (wt %) to about 5 wt %, based on the total weight of the polyester, of an epoxide additive comprising a epoxide compound with at least 2 epoxy groups per molecule. The fibers and films optionally may contain up to about 6 weight %, based on the total weight of the polyester, of a hindered phenol, phosphorus-containing, or sulfur-containing antioxidant to provide additional stability. The fiber compositions may take any of the following forms, namely monofilaments, multifilaments, tows, staple fibers, yarns, cords, woven knitted and tufted fabrics, nonwoven fabrics, melt-blown fabrics, spunbonded fabrics, composites, and laminates. Because of their high temperature resistance, the stabilized fibers are useful in industrial applications such a dryer felts of paper making machines, steamer belts, filters for hot air and hot liquid filtration, electrical motor housing, "breather fabrics" used in the production of vacuum bonded structural composites, high temperature insulation, and food processing under elevated temperatures. Similarly, the stabilized films of the present invention are useful for packaging applications, membranes, and as supports for biomaterials, air purification media, and chromatography. The term "degradation", as used herein, means a loss of inherent viscosity and tensile strength of the polymer over time as a result of exposure to high temperature with or without moisture present. Thus, terms such as "high temperature resistance", "heat stability", "temperature stability", "resistance to degradation", etc., refer to polymer, fiber, and film compositions that show a reduced loss of inherent viscosity or tensile strength over similar compositions at elevated temperatures, with or without moisture or air present. By the term "elevated temperatures", as used herein, it is meant temperatures in the range of 80 to 210° C. Representative temperatures within this range where our novel fibers show increased temperature stability are 126° C., 148° C. and 205° C.

The fibers and films of the present invention comprise polyesters prepared from dicarboxylic and diol residues. The term "polyester", as used herein, encompasses both "homopolymers" and "copolymers" and means a synthetic polymer prepared by the polycondensation of dicarboxylic acids with dihydro alcohols. The term "residue", as used herein, means any repeating organic structure incorporated into the polymer through a polycondensation reaction. Thus, the dicarboxylic acid residue may be derived from a dicarboxylic acid or its associated esters, salts, anhydrides, or mixtures thereof. As used herein, therefore, the term dicarboxylic acid is intended to include dicarboxylic acids and any derivative of a dicarboxylic acid, including its associated esters, half-esters, salts, half-salts, anhydrides, mixed anhydrides, or mixtures thereof, useful in a polycondensation process with a diol to make a high molecular weight

polyester. One or more dicarboxylic residues may be used. The dicarboxylic acid component, a total of 100 mole %, may comprise about 60 to 100 mole % of a first dicarboxylic acid residue from the residues of terephthalic acid, naphthalenedicarboxylic acids, cyclohexanedicarboxylic acids, or mixtures thereof. Preferably the first dicarboxylic acid residue will comprise about 80 to 100 mole % and, more preferably, from about 90 to 100 mole % of the dicarboxylic acid residues. Examples of naphthalenedicarboxylic acids which may be used in our invention include 1,2-naphthalenedicarboxylic acid, 1,3-naphthalenedicarboxylic acid, 1,4-naphthalenedicarboxylic acid, 1,5-naphthalenedicarboxylic acid, 1,6-naphthalenedicarboxylic acid, 2,4-naphthalenedicarboxylic acid, 2,5-naphthalenedicarboxylic acid, 2,6-naphthalenedicarboxylic acid, 2,7-naphthalenedicarboxylic acid, 2,8-naphthalenedicarboxylic acid, their associated esters, or mixtures thereof. The preferred naphthalenedicarboxylic acid is 2,6-naphthalenedicarboxylic acid. Examples of cyclohexanedicarboxylic acids are 1,2-cyclohexanedicarboxylic acid, 1,3-cyclohexanedicarboxylic acid, and 1,4-cyclohexanedicarboxylic acid. The preferred cyclohexane dicarboxylic acid is 1,4-cyclohexanedicarboxylic acid. The cycloaliphatic acids, for example, 1,3- and 1,4-cyclohexanedicarboxylic acids, may be present as their pure cis or trans isomers or as a mixture of cis and trans isomers. The preferred first dicarboxylic acid residue is terephthalic acid.

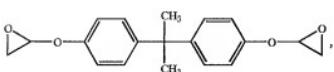
The first dicarboxylic acid residue may be modified with from 0 to about 40 mole % of a second dicarboxylic acid residue comprising residues from aromatic dicarboxylic acids containing from about 8 to about 16 carbon atoms, aliphatic dicarboxylic acids containing about 4 to about 16 carbon atoms, cycloaliphatic dicarboxylic acids containing from about 6 to about 16 carbon atoms, or mixtures thereof. Non-limiting examples of modifying dicarboxylic acids are fumaric, succinic, adipic, glutaric, azelaic, sebacic, isophthalic, resorcinolidaetic, 1,2-cyclobutanedicarboxylic acid, 1,3-cyclobutanedicarboxylic acid, 2,2,4,4-tetramethyl-1,3-cyclobutanedicarboxylic acid, diglycolic, 4,4'-oxybis [benzoic], biphenylcarboxylic, 4,4'-methylenebibenzoic, trans-4,4'-stilbenedicarboxylic, and sulfoisophthalic acids. A preferred second dicarboxylic acid residue is from isophthalic acid.

The diol residues comprise about 50 to 100 mole % of a first diol residue selected from 1,3-cyclohexanedimethanol, 1,4-cyclohexanedimethanol, 1,3-propanediol, and mixtures thereof; and from 0 to about 50 mole % of a second diol residue selected from aliphatic diols containing from 2 to about 16 carbon atoms, cycloaliphatic diols containing from about 6 to about 16 carbon atoms, and mixtures thereof.

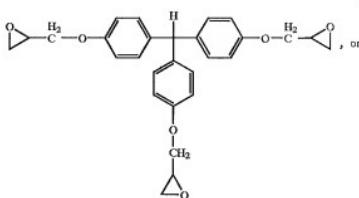
Preferably, the first diol residue may comprise about 70 to 100 mole % or, more preferably, from about 90 to 100 mole % of the diol residues. The cycloaliphatic diols, for example, 1,3- and 1,4-cyclohexanedimethanol, may be present as their pure cis or trans isomers or as a mixture of cis and trans isomers. As used herein, the term "diol" is synonymous with the term "glycol" and means any dihydric alcohol. The preferred first diol residue is from 1,4-cyclohexanedimethanol. Non-limiting examples of second diol residues are residues from ethylene glycol, neopentyl glycol, 1,3-propanediol, 1,4-butanediol, 1,5-pentanediol, 1,6-hexanediol, 2,2-dimethyl-1,3-propanediol, 1,8-octanediol, 1,10-decanediol, diethylene glycol, and 2,2,4,4-tetramethyl-1,3-cyclobutanediol. The preferred diols residues are from neopentyl glycol, 1,3-propanediol, and 1,6-hexanediol with ethylene glycol being most preferred.

The polyester is stabilized by the addition of about 0.05 weight % (abbreviated herein as "wt %") to about 5 wt %, based on the total weight of the polyester, of an epoxide additive comprising a epoxide compound or mixture of epoxide compounds with at least 2 epoxy groups per molecule. A representative concentration of epoxide additive is from about 0.05 wt % to about 2 wt %. More preferably, the concentration of epoxide additive is from about 0.1 to about 1 wt %, and most preferably, from about 0.2 to about 0.5 wt %. The epoxide additive may be any epoxide compound containing at least 2 epoxy groups but it is preferable that the epoxid additive have low volatility under melt processing or polymerization conditions of temperature and pressure. The terms "epoxide", "epoxide compound", "epoxide additive", "epoxy compound", and "glycidyl compound" as used herein, mean any organic compound, mixtures of organic compounds, polymers, or oligomers containing 1 or more oxirane rings and is intended to encompass compositions or formulations containing epoxide compounds or mixtures of epoxide compounds. The preferred epoxide additives contain compounds with at least 2 epoxy groups per molecule and preferably 3 or more epoxy groups. Preferably, the epoxide additive is selected from aromatic hydrocarbon monomers having at least 2 epoxide groups, oligomers and polymers of from 2 to 100 monomer units and having at least 2 epoxide groups, and mixtures thereof. For example, the epoxide compound may contain a plurality of 1,2-epoxide groups derived from the reaction of a polyfunctional active hydrogen containing compound with an excess of an epiphthaloydin under basic conditions. When the active hydrogen compound is a polyhydric alcohol or phenol, the resulting epoxide composition contains glycidyl ether groups. A preferred group of polyglycidyl compounds are made via condensation reactions with 2,2-bis-(4-hydroxyphenyl)propane, also known as bisphenol A, and have structures (I-III) such as the following:

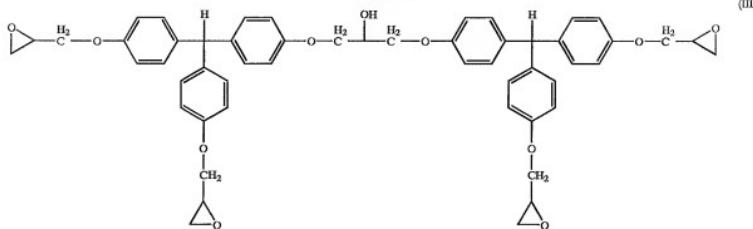
(I)



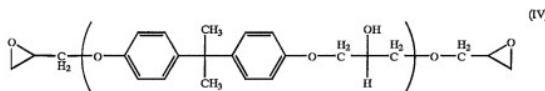
(II)



-continued



Oligomers or polymers incorporating structures (I-III) as monomers are also preferred as epoxide additives. The preferred epoxide additives may also comprise bisphenol A epoxy resins, i.e., oligomers or polymers having the formula (IV):



wherein n is 2 to about 100. Many of these epoxide additives are commercially available, for example "DER 331", "DER 332", "DER 334", and "XD9053.03" (Epoxy D in the examples, a trifunctional aromatic epoxy with molecular weight 460) from Dow Chemical Company (or, more recently, from Ciba-Geigy); and "Epon 828", "Epon 1004", "Epon 1010", and "Epon 1001F" (Epoxy B in the examples, a difunctional long chain epoxy compound supplied by Shell Chemical Co).

Other polyfunctional active hydrogen compounds can be used to make polyglycidyl adducts suitable for use in the practice of this invention. These include amines, amino alcohols and polycarboxylic acids. Adducts derived from amines and amino phenols include N,N-diglycidyl propylaniline, N,N,N',N'-tetraglycidyl-4,4'-diaminodiphenyl methane, N,N,N',N'-triglycidyl-4-aminophenol or N,N'-dimethyl-N,N'-diglycidyl-4,4'-diaminodiphenylmethane. Polyepoxides which are polyglycidyl esters of 4,4'-dihydroxy diphenyl methane, 4,4' dihydroxy diphenyl sulfone or tris(4-hydroxyphenyl)methane are useful in this invention.

Glycidyl esters of carboxylic acids may be used also in the present invention. Such glycidyl esters include, for example, diglycidyl phthalate and diglycidyl adipate. Polyepoxides prepared from polyols such as pentaerythritol, glycerol, butanediol or trimethylol propane and an epichlorohydrin are also useful. In addition, polyepoxides such as triglycidyl cyanurates and isocyanurates, N,N-diglycidyl oxamides, N,N-diglycidyl derivatives of hydantoins, and diglycidyl esters of cycloaliphatic dicarboxylic acids, and diglycidyl thioesters of polythiols are useful.

Other epoxy-containing materials are copolymers of acrylic acid esters of glycidol such as glycidyl acrylate and glycidyl methacrylate with one or more copolymerizable vinyl compounds. Examples of such copolymers are 1:1 styrene-glycidyl methacrylate, 1:1 methylmethacrylate-glycidyl acrylate and 62.5:24:13.5 methylmethacrylate: ethyl acrylate: glycidyl methacrylate.

Many suitable polyglycidyl compounds are available commercially. In addition to the bisphenol A epoxy resins mentioned above, these include 1,4-butanediol diglycidyl ether (e.g., "Araldite RD-2" from Ciba-Geigy Corporation), polyglycidyl ethers of phenolformaldehyde novolak (e.g.,

"DEN-A31" and "DEN-438" from Dow Chemical Co.), polyglycidyl ethers of a cresol-formaldehyde novolak resin (e.g., "Araldite® ECN 1299", referred to as "Epoxy A" in the examples), and "ECN-1273" (each from Ciba-Geigy Corporation), N,N-diglycidyl derivative of dimethyl hydian (e.g., "XB-2793" from Ciba Geigy Corporation), resorcinol diglycidyl ether (e.g., "Kopoxite" from Koppers Co., Inc.) and a methylolated bisphenol A epoxy resin (e.g.,

"Apogen 101" made by Schaefer Chemical Co.). Preferred epoxide additives are polyglycidyl ethers of a phenol-formaldehyde novolak resin, polyglycidyl ethers of a cresol-formaldehyde novolak resin (e.g., "Araldite® ECN 1299"), tris(4-glycidyloxyphenyl)methane, oligomers thereof, or polymers thereof, with polyglycidyl ethers of a cresol-formaldehyde novolak being particularly preferred.

Our novel polyester fibers or films may optionally contain up to about 6 wt %, based on the total weight of the polyester, of hindered phenol, phosphorus-containing, or sulfur-containing antioxidants, many of which are commercially available. For example, one suitable hindered phenol is tetrakis[methylene 3-(3', 5'-di-tert-butyl-4'-hydroxyphenyl)propionate]methane, which is Irganox® 1010 antioxidant by Ciba-Geigy. Other hindered phenols useful in the present invention include 1,3,5-tris(3,5-di-tert-butyl-4-hydroxybenzyl)-5-triazine-2,4,6-(1H, 3H, 5H)trione; 3,5-di-tert-butyl-4-hydroxyhydrocinnamic acid triester with 1,3,5-tris(2-hydroxyethyl)S-triazine-2,4,6-(1H, 3H, 5H)-trione; octadecyl 3,5-di-tert-butyl-4-hydroxyhydrocinnamate; thiobisdiethylene bis(3,5-di-tert-butyl-4-hydroxyhydrocinnamate); N,N'-hexamethylene bis(3,5-di-tert-butyl-4-hydroxy-hydrocinnamamide); 1,6-hexamethylene bis(3,5-di-tert-butyl-4-hydroxyhydrocinnamate), 1,3,5-trimethyl-2,4,6-(n-octylthio)-6-(4hydroxy-3,5-di-tert-butylamino)-1,3,5-triazine; n-octadecyl 3,5-di-tert-butyl-4-hydroxyhydrocinnamate; 1,3,5-tris(4-tert-butyl-3-hydroxy-2,6-dimethylbenzyl)-1,3,5-triazine-2,4,6-(1H, 3H, 5H)trione;

2,2'-methylenebis(4-ethyl-6-tert-butylphenol); 2,2'-methylenebis(4-methyl-6-tert-butylphenol); 4,4'-methylenbis(2,6-di-tert-butylphenol); 4,4'-thiobis(6-tert-butyl-o-cresol); 3:1 condensate of 3-methyl-6-tert-butylphenol and crotonaldehyde; 4,4'-butyldienebis(6-tert-butyl-m-cresol); 3,5-di-tert-butyl-4-hydroxybenzyl ether; 2,2'-oxa-mido-bis(ethyl-3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate; stearlyl  $\beta$ -(3,5-di-tert-butyl-4-hydroxyphenyl)propionate; distearyl 3-methyl-4-hydroxy-5-tert-butylbenzyl malonate; 4,4'-propylmethylenbis(2-tert-butyl-5-methylphenol); 2,2'-propylmethylenbis(4,6-dimethylphenol); 2,2'-methylene-bis(4,6-di-tert-butylphenol); 1,4-bis[3,(5-di-tert-butyl-4-hydroxybenzyl)-2,3,5,6-tetrahydrobenzene]; 1,1-bis[3'-cyclohexyl-4'-hydroxyphenyl]cyclohexane; 2,6-bis(2-hydroxy-3-tert-butyl-5-methylphenyl)-4-methylphenol; 2,4,6-tris(B(3',5'-hydroxyphenyl)ethyl)-1,3,5-triazine; and 2,4,6-tris(3',5-di-tert-butyl-4-hydroxybenzyl)phenol.

The phosphorus-containing antioxidant may be either a phosphite or a phosphonite. Examples of such materials are "Ultranox 620" phosphite, "Ultranox 633" phosphite, (General Electric Chemicals), "Irgafos 168" phosphite (Ciba-Geigy Corporation), 2,2'-ethylenedibis(4,6-di-tert-butylphenyl)fluorophosphite ("Ethanox 398" phosphite, Albemarle Corporation), 2,2'-Ethylenedibis(4,6-di-tert-butylphenyl)fluorophosphonite ("Ethanox 398" phosphonite, Albemarle Corporation), "Sandostab PEPO" phosphonite (Sandoz Chemicals), and a combination of distearyl or diarylaryl thioldipropionate with 1,3,5-dimethyl-2,4,6-tris(3,5-di-tert-butyl-4-hydroxybenzyl)benzene ("Ethanox 330", available from Albemarle Corporation). For the present invention, representative concentrations of antioxidants are from 0 to about 6 wt % and from about 0.1 to about 4 wt %. Preferably, these antioxidants are present at concentrations ranging from about 0.1 to about 2 wt %, more preferably from about 0.2 to about 1 wt %, and most preferably from about 0.2 to about 0.5 wt % based on the total weight of the polyester.

A preferred embodiment of the present invention is a polyester fiber comprising: i) dicarboxylic acid residues comprising about 60 to 100 mole % of terephthalic acid and from 0 to about 40% of isophthalic acid; ii) diol residues comprising about 50 to 100 mole % of a first diol residue comprising 1,4-cyclohexanedimethanol; and from 0 to about 50 mole % of a second diol residue comprising aliphatic diols containing from 2 to about 16 carbon atoms; and iii) about 0.05 wt % to about 2 wt %, based on the total weight of the polyester, of an epoxide additive comprising a epoxide compound with at least 2 epoxy groups per molecule. The polyester preferably has a glass transition temperature ("T<sub>g</sub>") of greater than or equal to 85° C. Preferably, the first diol residue may comprise about 70 to 100 mole % or, more preferably, from about 90 to 100 mole % of the diol residues. The concentration of epoxy compound may be from about 0.1 to about 1 wt % or, preferably, from about 0.2 to about 0.5 wt %. The polyester fiber may contain from 0 wt % to about 6 wt % of an antioxidant based on the total weight of the polyester. If an antioxidant is used, it typically comprises about 0.1 to about 2 wt % or, more typically, about 0.2 to about 1 wt % of the total weight of the polyester fiber. Most preferably, the antioxidant comprises about 0.5 wt % of a hindered phenol and about 0.5 wt % of a phosphite or phosphonite. More preferably, the dicarboxylic acid residues comprise from about 90 to 100 mole % terephthalic acid and from about 0 to about 10 mole % isophthalic acid; the diol residues comprise about 100 mole % 1,4-cyclohexanedimethanol thereof; and the epoxide additive comprises about 0.5 wt % of a polyglycidyl ether of a cresol-formaldehyde novolac resin. Most preferably, the dicarboxylic acid residue comprises about 95 mole % terephthalic acid and about 5 mole % isophthalic acid, and

the epoxide additive comprises about 0.5 wt % of a polyglycidyl ether of a cresol-formaldehyde novolac resin.

The polyester fiber may also comprise a dicarboxylic acid residue comprising about 100 mole % terephthalic acid and a diol residue comprising about 100 mole % 1,4-cyclohexanedimethanol, or mixtures thereof. The polyester is melt blended with about 0.05 wt % to about 2 wt %, based on the total weight of the polyester, of an epoxide additive comprising a epoxide compound or mixture of epoxide compounds with at least 2 epoxy groups per molecule and, optionally, from 0 wt % to about 6 wt % of an antioxidant based on the total weight of the polyester, and continuous strands of filaments are melt spun from the blend. The polyester preferably has a glass transition temperature ("T<sub>g</sub>") of greater than or equal to 85° C. The concentration of epoxy compound may be from about 0.1 to about 1 wt % or, preferably, from about 0.2 to about 0.5 wt %. Most preferably, the epoxide additive comprises about 0.5 wt % of a polyglycidyl ether of a cresol-formaldehyde novolac resin. If an antioxidant is used, it typically comprises about 0.1 to about 2 wt % or, more typically, about 0.2 to about 1 wt % of the total weight of the polyester. Preferably, the antioxidant comprises about 0.5 wt % of a hindered phenol and about 0.5 wt % of a phosphite or phosphonite.

For the purposes of this invention, the term "fiber" refers to a shaped polymeric body of high aspect ratio capable of being formed into two or three dimensional articles such as woven or nonwoven fabrics. The term "polyester fiber" means fibers prepared from polyester polymers that may include the various antioxidants, pigments, and additives described herein. In addition, fiber refers to filaments that may take any of the various forms well known to persons skilled in the art, namely monofilaments, multifilaments, tows, staple or cut fibers, staple yarns, cords, woven, tufted, and knitted fabrics, nonwoven fabrics, including melt blown fabrics and spunbond fabrics, and multilayer nonwovens, laminates, and composites from such fibers. Most fiber forms are heatset. The fibers of the present invention may be a mono filament, multifilament, or bicomponent fiber. Our novel fibers may be produced as a staple, yarn, cord, or a direct spun, nonwoven fabric.

The monofilament fibers generally range in size from about 20 to about 8000 denier per filament (abbreviated herein as "d/f") and are particularly useful in paper machine clothing applications. The preferred fibers will have d/f values in the range of about 500 to about 5000. Such monofilaments may be in the form of unicomponent or bicomponent fibers. Bicomponent fibers may have sheath/core, side by side, or other configurations known to persons skilled in the art. Other multicomponent configurations are also possible. The process of preparing bicomponent fibers also is well known and is described in U.S. Pat. No. 3,589,956. In a bicomponent fiber, the stabilized polyester fibers of this invention will be present in amounts of about 10 to about 90 wt % and will generally be used in the sheath portion of sheath/core fibers. The other component may be from a wide range of other polymeric materials including but not limited to polyesters such as PET, PBT, PTT, polyalactides and the like as well as polyolefins, cellulose esters, and polyamides. Side by side combinations with significant differences in thermal shrinkage can be utilized for the development of a spiral crimp. If crimping is desired, a saw tooth or stuffer box crimp is generally suitable for many applications. If the second polyester is in the core of a sheath/core configuration, such a core optionally may be stabilized.

The multifilament fibers of our invention will preferably range in size from about 2 micrometers for melt blown webs, about 0.5 to about 50 d/f for staple fibers, and up to about 5000 d/f for monofilament fibers. Multifilament fibers may also be used as crimped or uncrimped yarns and tows. Fibers

used in melt spun and melt blown web fabric may be produced in microdenier sizes.

The polyesters of the instant invention are readily prepared from the appropriate dibasic acids, esters, anhydrides, or salts, and the appropriate diol or diol mixtures using typical polycondensation reaction conditions. They may be made by continuous, semi-continuous, and batch modes of operation and may utilize a variety of reactor types. Examples of suitable reactor types include, but are not limited to, stirred tank, continuous stirred tank, slurry, tubular, wiped-film, falling film, or extrusion reactors. The term "continuous" as used herein means a process wherein reactants are introduced and products withdrawn simultaneously in an uninterrupted manner. By "continuous" it is meant that the process is substantially or completely continuous in operation and is to be contrasted with a "batch" process. "Continuous" is not meant in any way to prohibit normal interruptions in the continuity of the process due to, for example, start-up, reactor maintenance, or scheduled shut down periods. The term "batch" process as used herein means a process wherein all the reactants are added to the reactor and then processed according to a predetermined course of reaction during which no material is fed or removed into the reactor. The term "semicontinuous" means a process where some of the reactants are charged at the beginning of the process and the remaining reactants are fed continuously as the reaction progresses. Alternatively, a semicontinuous process may also include a process similar to a batch process in which all the reactants are added at the beginning of the process except that one or more of the products are removed continuously as the reaction progresses. The process is operated advantageously as a continuous process for economic reasons and to produce superior coloration of the polymer as the polyester may deteriorate in appearance if allowed to reside in a reactor at an elevated temperature for too long a duration.

In forming the polyesters of the invention, the reaction of the diol component and the dicarboxylic acid component may be carried out using conventional polyester polymerization conditions. For example, when preparing the polyesters and copolymers by means of an ester interchange reaction, i.e., from the ester form of the dicarboxylic acid components, the reaction process may comprise two steps. In the first step, the diol component and the dicarboxylic acid component, such as, for example, dimethyl terephthalate, are reacted at elevated temperatures, typically, about 180° C. to about 280° C. at pressures ranging from about 0.0 kPa gauge to about 414 kPa gauge (60 pounds per square inch, "psig"). Preferably, the temperature for the ester interchange reaction ranges from about 190° C. to about 240° C. while the preferred pressure ranges from about 103 kPa gauge (15 psig) to about 276 kPa gauge (40 psig). Thereafter, the reaction product is heated under higher temperatures and under reduced pressure to form polyester with the elimination of diol, which is readily volatilized under these conditions and removed from the system. This second step, or polycondensation step, is continued under higher vacuum and a temperature which generally ranges from about 240° C. to about 300° C., preferably about 250° C. to about 290° C. and most preferably about 270° C. to about 285° C., until a polymer having the desired degree of polymerization, as determined by inherent viscosity, abbreviated herein as "I.V." is obtained. The polycondensation step may be conducted under reduced pressure which ranges from about 53 kPa (400 torr) to about 0.013 kPa (0.1 torr). The presence of a suitable catalyst greatly increases the rate of the above reactions.

To ensure that the reaction of the diol component and dicarboxylic acid component by an ester interchange reaction mechanism is driven to completion, it is preferred to employ 3 moles and more preferably about 2.3 to about 2.6 moles of diol component to one mole dicarboxylic acid component. Persons of skill in the art will understand, however, that the ratio of diol component to dicarboxylic acid component is generally determined by the design of the reactor in which the reaction process occurs.

In the preparation of polyester by direct esterification, i.e., from the acid form of the dicarboxylic acid component, copolymers are produced by reacting the dicarboxylic acid or a mixture of dicarboxylic acids with the diol component or a mixture of diol components. The reaction is conducted at a pressure of from about 7 kPa gauge (1 psig) to about 1379 kPa gauge (200 psig), preferably less than 689 kPa (100 psig) to produce a low molecular weight, linear or branched polyester product having an average degree of polymerization of from about 1.4 to about 10. The temperatures employed during the direct esterification reaction typically range from about 1 80° C. to about 280° C., more preferably ranging from about 220° C. to about 270° C. This low molecular weight polymer may then be polymerized by a polycondensation reaction.

To ensure that the reaction of the diol component and dicarboxylic acid component by a direct esterification reaction mechanism is driven to completion, it is preferred to employ about 3.0 to about 10.5 moles diol component to one mole dicarboxylic acid component. Persons of skill in the art will understand, however, that the ratio of diol component to dicarboxylic acid component will be determined by the design of the reactor in which the reaction process occurs.

Lower I.V. copolymers are generally obtained by employing shorter residence times or slow reaction rates as compared to processes for forming higher I.V. copolymers. For example, the reaction rate can be slowed by reducing the reaction temperature, reducing the catalyst concentration, by increasing the absolute pressure in the reactor, or by a combination of these factors.

A variety of catalyst systems are useful in promoting the reaction of the diol component and the dicarboxylic acid component. Typically a catalyst system will contain one or more catalysts and catalyst inhibitors. Well known catalysts include, but are not limited to, compounds containing titanium, manganese, zinc, cobalt, antimony, gallium, lithium, calcium, silicon, and germanium. Generally, the catalyst comprises compounds which contain titanium, manganese and/or zinc and mixtures thereof. While the amounts of the individual catalysts in the catalyst system will vary, it is desired that the total amount of catalyst in the catalyst system be below about 125 ppm, preferably below about 100 ppm and most preferably below about 80 ppm. The "ppm" for the catalyst and the catalyst inhibitor described below, refers to the weight of the element referred to and is based upon the weight of the final copolyester product.

The polyester fibers and films of this invention also may contain other conventional additives and ingredients which do not deleteriously affect their end use. For example, additives such as fillers, surface friction modifiers, light and heat stabilizers, extrusion aids, antistatic agents, colorants, dyes, pigments, hydrophobic and hydrophilic enhancers, viscosity modifiers, slip agents, tougheners, adhesion promoters, and the like may be used. Preferably, colorants, sometimes referred to as toners, may be added to impart a desired neutral hue and/or brightness to the resulting copolyester. When colored polyesters are desired, pigments or colorants may be included in the reaction mixture during the

reaction of the diol component and the dicarboxylic acid component or they may be melt blended with the preformed polyester. A preferred method of including colorants is to use a colorant having thermally stable organic colored compounds having reactive groups such that the colorant is copolymerized and incorporated into the copolyester to improve the hue of the polyester. For example, colorants such as dyes possessing reactive hydroxyl and/or carboxyl groups, including, but not limited to, blue and red substituted anthraquinones, may be copolymerized into the polymer chain. When dyes are employed as colorants, they may be added to the copolyester reaction process after an ester interchange or direct esterification reaction.

Alternatively, inorganic pigments, such as titanium dioxide and cobalt containing materials, may be added to the reaction. Advantageously when a catalyst material contains cobalt, the cobalt may also act as a colorant. Care must be taken to control the level of cobalt in order to avoid leveling in the copolymers of the invention. To control the level of dinginess, cobalt may be employed in an amount ranging up to about 90 ppm.

The inherent viscosity of the polyester for the present invention will generally be in the range of about 0.3 to about 2.0 and is generally determined in a 0.5 wt % solution in a 60/40 phenol/tetrachloroethane mixture. When making fine denier melt blown or spunbonded fibers, low I.V. polymers having I.V. values of about 0.3 to about 0.6 are preferred. However for the mono- and multifilament fibers, higher I.V. polymers in the range of about 0.45 to about 1.25 are preferred.

Our invention also provides a process for stabilizing polyester fibers comprising: i) melt blending a) a polyester comprising about 60 to 100 mole % of a dicarboxylic acid residue selected from the group consisting of terephthalic acid, naphthalenedicarboxylic acids, cyclohexanedicarboxylic acids, and mixtures thereof; about 50 to 100 mole % of a diol residue selected from the group consisting of 1,3-cyclohexanedimethanol, 1,4-cyclohexanedimethanol, 1,3-propanediol, and mixtures thereof; and b) about 0.05 wt % to about 5 wt %, based on the total weight of the polyester, of an epoxide additive comprising a epoxide compound with at least 2 epoxy groups per molecule; and ii) melt spinning continuous strands of filaments. Up to about 6 wt %, based on the total weight of the polyester, of an antioxidant may be added to the polyester, either during polymerization or by melt-blending the antioxidant into the polyester. The terms "melt spinning" and "extrusion spinning" as used herein mean process wherein a polymer melt is forced under pressure or extruded through a spinnerette or spinning die and quenched to form strands of polymer filaments. Typically, about 0.05 wt % to about 2 wt % of epoxide additive may be used. More preferably, the concentration of epoxide additive is from about 0.1 to about 1 wt %, and most preferably, from about 0.2 to about 0.5 wt %. The first diol residue may comprise about 70 to 100 mole % or from about 90 to 100 mole % of the diol residues. Preferably, the dicarboxylic acid residue of our process comprises from about 95 to 100 mole % terephthalic acid and from about 0 to about 5 mole % isophthalic acid; the diol residue comprises about 100 mole % 1,4-cyclohexanedimethanol; and the epoxy comprises about 0.5 wt % of a polyglycidyl ether of a cresol-formaldehyde novolac resin. More preferably, the dicarboxylic acid residue comprises from about 95 mole % terephthalic acid and about 5 mole % isophthalic acid. Even more preferably, the epoxy comprises about 0.5 wt % of a polyglycidyl ether of a phenol-formaldehyde novolac resin. If an antioxidant is used, it typically comprises about 0.1 to about 2 wt % or, more typically, about 0.2 to about 1 wt % of the total weight of the polyester. Preferably, the antioxidant comprises about 0.5 wt % of a hindered phenol and about 0.5 wt % of a phosphite or phosphonite.

The polyester utilized by our novel process may also comprise a dicarboxylic acid residue comprising about 100 mole % terephthalic acid and a diol residue comprising about 100 mole % 1,4-cyclohexanedimethanol. The polyester is melt blended with about 0.05 wt % to about 5 wt %, based on the total weight of the polyester, of an epoxide additive comprising a epoxide compound with at least 2 epoxy groups per molecule and continuous strands of filaments are melt spun from the blend. Typically, about 0.05 wt % to about 2 wt % of epoxide additive may be used. More preferably, the concentration of epoxide additive is from about 0.1 to about 1 wt %, and most preferably, from about 0.2 to about 0.5 wt %. Preferably the epoxide additive comprises about 0.5 wt % of a polyglycidyl ether of a cresol-formaldehyde novolac resin. Optionally, from 0 wt % to about 6 wt % of an antioxidant based on the total weight of the polyester, may be added to polyester. Preferably, the antioxidant comprises about 0.5 wt % of a hindered phenol and about 0.5 wt % of a phosphite or phosphonite.

The polyester and epoxide additive may be mixed in batch, semicontinuous, or continuous processes as described above. It is preferred to meter in the epoxy component while extruding the polyester in either a single or twin screw extruder. Small scale batches may be readily prepared in any high-intensity mixing devices well-known to those skilled in the art, such as Banbury mixers, prior to melt-spinning fibers. The components preferably may also be blended in solution in an appropriate solvent. Another preferred technique is to prepare a master batch of polyester containing from about 5 to about 30 wt % epoxide additive and subsequently to let this master batch down to desired epoxy concentration in the same or different polyester.

The melt blending method includes blending the polyesters and epoxide additive at a temperature sufficient to melt the polyester. The blend may be cooled and pelletized for further use or the melt blend can be melt spun directly from this molten blend into fiber form. The term "melt" as used herein includes, but is not limited to, merely softening the polyester. For melt mixing methods generally known in the polymers art, see "Mixing and Compounding of Polymers" (I. Manas-Zloczower & Z. Tadmor editors, Carl Hanser Verlag Publisher, 1994, New York, N.Y.).

Our invention also provides a stabilized polyester film comprising i) a polyester comprising about 60 to 100 mole % of a dicarboxylic acid residue selected from the group consisting of terephthalic acid, naphthalenedicarboxylic acids, cyclohexanedicarboxylic acids, and mixtures thereof; about 50 to 100 mole % of a diol residue selected from the group consisting of 1,3-cyclohexanedimethanol, 1,4-cyclohexanedimethanol, 1,3-propanediol, and mixtures thereof; and ii) about 0.05 wt % to about 5 wt %, based on the total weight of the polyester, of an epoxide additive comprising a epoxide compound with at least 2 epoxy groups per molecule. Typically, the concentration of epoxide compound may be from about 0.1 to about 2 wt %, preferably, from about 0.1 to about 1 wt %, and, more preferably, from about 0.2 to about 0.5 wt %. The first diol residue may comprise about 70 to 100 mole % or from about 90 to 100 mole % of the diol residues. Preferably, the dicarboxylic acid residue of our film comprises from about 90 to 100 mole % terephthalic acid and from about 0 to about 5 mole % isophthalic acid, the diol residue comprises about 100 mole % 1,4-cyclohexanedimethanol, and the epoxy comprises about 0.5 wt % of a polyglycidyl ether of a phenol-formaldehyde novolac resin. More preferably, the dicarboxylic acid residue comprises from about 95 mole % terephthalic acid and about 5 mole % isophthalic acid, and most preferably the dicarboxylic acid residue comprises about 100 mole % terephthalic acid. Optionally, the film may contain from 0 wt % to about 6 wt % of an antioxidant based on the total weight of the polyester. If an antioxidant

is used, it typically comprises about 0.1 to about 2 wt % or, more typically, about 0.2 to about 1 wt % of the total weight of the polyester. Preferably, the antioxidant comprises about 0.5 wt % of a hindered phenol and about 0.5 wt % of a phosphite or phosphonite.

According to the invention, our novel polyester film may be produced as a monolayer or multilayer film and in a non-oriented or oriented state. The monolayer film may be produced by conventional extrusion or casting techniques. The multilayered films may be produced by conventional coextrusion, lamination, or the like. The readily crystallizable layer may have a layer of the heat-sealable layer applied to one or both sides. The film may be of any convenient thickness, but total thickness will normally be between about 5 and about 50 mil. Normally, the heat-sealing polyester in multilayered films will account for about 5-50% of the total thickness of the film.

A biaxial film may be obtained by conventional, known methods or methods well known to persons of ordinary skill in the art. For example, it can be obtained by forming an unstretched film and then, biaxially stretching the resulting unstretched film. The unstretched film having an intrinsic viscosity of 0.35 to 0.9 dL/g may be obtained by melt extruding a polyester into a film form, for example, from the melting point temperature of the polyester up to a temperature of about 70° C. above the melting point and solidifying, by quenching, the film. For the purposes of this invention, the melting point is determined by any means known in the art. The preferred method of determining melting point and glass transition temperature is by the differential scanning calorimetry (DSC) well known in the art. The melting point can be specifically defined in this context as the temperature of the highest peak on the endotherm of the plot produced via DSC.

The polyester film of the present invention is usually extruded in a form of a sheet, present on a casting drum, and after an amorphous sheet is made, the sheet is stretched and heat set to produce a biaxially stretched film. Preferably, polyester films of our invention are manufactured by forming a substantially amorphous film from the polyester defined in detail above and, optionally, annealing the film by heating it above its glass transition temperature to effect crystallization of the polyester. The annealing step may be performed by heating the substantially amorphous polyester film at a temperature of at least 80° C. for a period of time sufficient to impart to the resulting article a heat stability (in accordance with ASTM method D1637) of at least 70° C. The substantially amorphous polyester sheet is prepared by extruding or rolling the polyester into a sheet or film and then quenching the extruded or molded article by rapidly cooling it.

The rapid cooling can be accomplished by any method which provides for the removal of heat from the molten polyester at a rate sufficient to prevent significant crystallization of the polyester. The required heat removal can be accomplished by contacting the extruded or molded polyester melt with a cooled or chilled roll or mold, for example a roll or mold maintained at or below about 15° C. Alternatively, the polyester melt can be contacted with a cold gas to accomplish the necessary rapid cooling. The rapid cooling prevents significant crystallization and thereby permits the formation of an article having good clarity. Thicker articles require a greater heat transfer rate and, consequently, a more rigorous means of cooling to give a clear, substantially amorphous article. The rapid cooling may be effected simultaneously with a shaping step as occurs, for example, when an extruded cylinder of the polyester is enveloped by a chilled mold and the molten polyester is forced outwardly into the mold by means of a gas at superatmospheric pressure.

The unstretched film can be formed into a biaxially oriented film in accordance with any of biaxially oriented

film production methods which have been accumulated heretofore. For example, the unstretched film is stretched to 2.5 to 7.0 times in one direction (longitudinal or transverse direction) at a temperature of Tg-10° C. to about Tg+70° C. ("Tg" as used herein refers to the glass transition temperature of a polyester in ° C.) and then to 2.5 to 7.0 times in the direction perpendicular to the above direction (transverse direction when first stretched in the longitudinal direction) at the glass transition temperature up to a temperature of Tg+70° C. In this case, the area stretch ratio is preferably set to 9 to 32 times, more preferably 12 to 32 times. The stretching means may be either simultaneous biaxial stretching or sequential biaxial stretching. Further, the biaxially oriented film can be heat-set at a temperature of Tg-70° C. to Tm.

Alternatively, polyester film may be produced as heat-shrinkable films and sheet. Heat-shrinkable plastic films are used for labelling, protection, parcelling, and wrapping of glass, metal, ceramic and plastic bottles, boxes, cans, pipes, and wood. For example, heat-shrinkable films are widely used as tamper evident labels on food and pharmaceutical products, as primary labels on plastic containers such as soft drink bottles, and protective wraps for medicines and dry cell batteries.

The present invention is illustrated by the following examples.

## EXAMPLES

### Testing Procedures

The following polyester polymers were used to prepare fiber samples:

#### Polymer Monomer Components (percentages as mole %)

PET	100% terephthalic acid, 100% ethylene glycol
PETO	100% terephthalic acid, 31%, ethylene glycol, 69% 1,4-cyclohexanedimethanol
PCT	100% terephthalic acid, 100% 1,4-cyclohexanedimethanol
PCTA	95% moleterephthalic acid, 5% isophthalic acid, 100%, 1,4-cyclohexanedimethanol
PCTO	100% terephthalic acid, 81% 1,4-cyclohexanedimethanol, 19% ethylene glycol

All fibers were tested for single filament tensile properties (Instron Test Equipment), strand (10 filaments) tensile properties, strand tensile properties after exposure to dry heat at 401° F. (205° C.), except for PETG samples that were tested at 194° F. (90° C.). Seven samples of each fiber sample were placed in an oven at the appropriate temperature test conditions. Samples were removed after 1, 2, 4, 6, 8, 10, and 24 hours. Strand tensile properties were determined on each of these aged samples.

For determination of moist heat stability, strand samples were also exposed in an autoclave containing steam at 298° F. (148° C.), except PETG samples that were tested at 259° F. (126° C.). Two samples of each fiber sample were exposed to these conditions for 12 and 24 hours. Treated samples were tested for tensile properties.

### Example 1

#### PCT Fibers Containing Epoxy Compounds

PCT Polyester (I.V. 0.77 dL/g) was compounded at 572° F. (300° C.) on a 40 mm twin screw extruder. With 2.0% of the epoxide additive (Dow XD, 9053.03 Epoxy, referred to as Epoxy D in Table I). Salt and pepper blends with additional virgin resins were then prepared to contain 0, 0.1, 0.2, 0.5, 1.0 and 2.0 weight % epoxy compound. These blends were dried at 248° F. (120° C.) for 4 hours and then were melt extruded into multifilament fibers using a spinnerette having

10 holes (0.3 mm round orifices), at 590° F (310° C.), at a take-up speed of 500 meters/minute and an extrusion rate of 1 pound an hour. These as-spun fibers were about 10 denier/filament (d/f). The as-spun fibers were subsequently drawn through a chamber heated to 284–302° F (140–150° C.) using a single-stage drafting process to provide a 3:1 draft ratio and were relaxed heatset at 180° C. The fibers were wound on packages and had a final d/f of about 3.5 (for PCT polyester, fiber heatsetting temperatures up to 205 C are practiced). Results of Instron tensile measurements are shown in Table 1 and indicate that inclusion of the epoxide additive improves the dry heat stability of PCT fibers and that there is an optimum level. The hydrolytic stability of the fibers was considered good at all levels of epoxide additive.

TABLE 1

Sample	Tenacity of Stabilized PCT Polyester Fibers Before and After Accelerated Aging					
	A	B	C	D	E	F
Wt % Epoxy D	0.0	0.1	0.2	0.5	1.0	2.0
As Spun PCT Filament	2.7	3.0	2.8	2.9	2.7	2.4
As 10-fil Spun PCT Strands	2.5	2.6	2.6	2.7	2.4	2.4
Aged (Temp./Time)	Strand Dry-Heat Stability (Tenacity, g/denier)					
401° F (205° C)/1 hour	2.1	2.5	2.5	2.4	2.3	1.8
401° F (205° C)/2 hour	1.8	2.2	2.4	2.5	2.3	1.5
401° F (205° C)/4 hour	1.3	2.1	2.2	2.6	2.3	1.8
401° F (205° C)/6 hour	0.9	1.5	1.8	2.0	2.2	1.7
401° F (205° C)/8 hour	0.6	1.7	1.5	2.3	2.0	1.7
401° F (205° C)/10 hour	0.7	0.8	1.5	1.8	1.8	1.5
401° F (205° C)/24 hour	0.4	0.8	0.7	1.0	0.8	0.8
	Strand Moist-Heat Stability (Tenacity, g/denier)					
298° F (148° C)/12 hr Wet	1.9	2.3	2.3	2.5	2.3	2.2
298° F (148° C)/24 hr Wet	1.4	2.2	2.0	2.3	2.1	2.1

## Example 2

Polyester Fibers Containing Various Levels of Epoxy Compound (Table 2)

The following pellet samples of polyesters were compounded on a 40 mm twin screw extruder at 572° F (300° C) to contain selected epoxy compounds. These were then extruded in a second step into fibers and tested after aging under dry and wet conditions as described above. Pellet samples AA and BB were dried at 248° F (120° C) for 4 hours and then were melt extruded using a melt temperature of 536° F (280° C) as described in Example 1 to provide multifilament fibers with a denier of about 12 d/f. The as-spun fibers were subsequently drawn in a 158° F (70° C.) water bath and then through a chamber heated to 302–320°

F (150–160° C.) (2-stage drafting process) to provide a 4:1 draft ratio. The fibers were relaxed heatset at 150° C., wound on packages, and had a final denier of about 3.8 d/f.

Pellet samples CC and DD were dried at 122° F (50° C) for 4 hours and then extruded into multifilament fibers of about 10 d/f at a melt temperature of 509° F (265° C.) using the procedure described in Example 1. The as-spun fibers were subsequently drawn in a 158° F (70° C.) water bath, using a two-stage drafting process to provide a 3.25:1 draft ratio. The fibers were further drafted through a chamber heated to 194–212° F (90–100° C.) and relaxed heatset at 150° C. The fibers were wound on packages and had a final denier of about 3.5 d/f.

Pellet samples EE and FF were dried at 248° F (120° C.) for 4 hours and then melt spun at a melt temperature of 554° F (290° C.) using the process described in Example 1 to provide multifilament fibers of 9 d/f. The as-spun fibers were subsequently drawn through a chamber heated to 302–320° F (150–160° C.) (single stage drafting process) to provide a 3.2:1 draft ratio and relaxed heatset at 150° C. The fibers were wound on packages and had a final denier of about 3 d/f.

Pellet samples GG and HH were dried at 248° F (120° C.) for 4 hours and then were melt extruded at a melt temperature of 590° F (310° C.) using the procedure described in Example 1 to provide multifilament fibers of about 9 d/f. The as-spun fibers were subsequently drawn through a chamber heated to 302–320° F (150–160° C.), using a single stage drafting process, to provide a 3.2:1 draft ratio and relaxed heatset at 150° C. The fibers were wound onto packages and had a final denier of about 3.0 d/f.

Pellet samples II, JJ, KK, and LL were dried at 248° F (120° C) for 4 hours and then were melt extruded at a melt temperature of 590° F (310° C.) using the process described in Example 1 to provide multifilament fibers having a denier of about 9 d/f. The as-spun fibers were subsequently drawn through a chamber heated to 302–320° F (150–160° C.) using a single stage drafting process to provide a 3.2:1 draft ratio and relaxed heatset at 150° C. The fibers were wound onto packages and had a final denier of about 3 d/f.

This example shows that the dry oven aging performance of the fibers is improved with epoxy addition in the CHDM polymers (PCT, PCTG, and PCTA) whereas no corresponding improvement is observed for PET. The copolymers show a gradual transition with CHDM content. Hydrolytic stability is given by the autoclaving data, which shows the superiority of the CHDM polyesters, which is not reduced by the epoxy. Epoxy A has similar epoxy equivalent weight to Epoxy D in Example 1 whereas the higher level of Epoxy B must be used to achieve an equivalent concentration of functional groups.

TABLE 2

Sample	Tenacity (g/denier) of Various Polyester Fibers with Epoxy, before and after Accelerated Aging											
	AA	BB	CC	DD	EE	FF	GG	HH	II	JJ	KK	LL
Basic Resin	PET	PET	PETG	PETG	PCTG	PCTG	PCTA	PCTA	PCT	PCT	PCT	PCT
Epoxy Additive (wt %)	—	0.5 A	—	0.5 A	—	0.5 A	—	0.5 A	—	0.5 A	0.5 B	1.25 B
As Spun Filament	5.8	4.3	4.5	3.9	4.3	3.5	4.0	3.6	3.8	3.6	3.5	3.4
As Spun Strand	4.8	3.4	2.6	2.5	3.3	3.0	2.5	3.2	3.2	3.3	3.0	2.9

TABLE 2-continued

Sample	Tenacity (g/denier) of Various Polyester Fibers with Epoxy, before and after Accelerated Aging											
	AA	BB	CC	DD	EE	FF	GG	HH	II	JJ	KK	LL
Aged (Dry)	Dry-Heat Stability (Strand Tenacity in g/denier)											
Oven Temp. ° F. (° C.)	401 (205)	401 (205)	194 (90)	194 (90)	401 (205)							
Time												
1 Hour	4.7	4.4	2.7	2.6	1.5	2.5	2.8	3.0	2.9	3.2	3.2	3.0
2 Hours	4.8	3.6	2.5	2.7	0.5	2.7	2.5	3.0	2.5	3.2	3.2	3.0
4 Hours	5.0	3.3	2.7	2.5	Fail	1.3	2.0	2.8	2.2	2.9	2.6	3.2
6 Hours	4.0	3.2	3.0	2.8	Fail	0.9	1.8	2.7	2.6	2.5	2.9	2.9
8 Hours	3.8	3.5	2.9	2.7	Fail	0.9	1.6	2.4	1.9	2.5	2.9	2.8
10 Hours	5.3	3.1	2.9	2.7	Fail	0.3	1.4	2.5	1.5	2.3	2.6	2.5
24 Hours	3.0	2.6	3.0	2.6	Fail	Fail	0.8	0.7	1.4	1.7	1.8	2.0
Aged (Wet)	Moist-Heat Stability (Strand Tenacity in g/denier)											
Autoclave Temp. ° F. (° C.)	298 (148)	298 (148)	259 (126)	259 (126)	298 (148)							
Time												
12 Hours	3.4	2.3	Fail	Fail	2.9	1.9	3.2	2.9	3.1	3.0	3.1	2.5
24 Hours	1.6	0.5	Fail	Fail	1.1	Fail	3.0	2.7	2.7	2.8	2.8	2.8

We claim:

1. A polyester fiber comprising:
  - i) dicarboxylic acid residues comprising about 60 to 100 mole % of a first dicarboxylic acid residue selected from the group consisting of terephthalic acid, naphthalene-dicarboxylic acids, cyclohexanedicarboxylic acids, and mixtures thereof; and from 0 to about 40% of a second dicarboxylic acid residue selected from the group consisting of aromatic dicarboxylic acids containing from about 8 to about 16 carbon atoms, aliphatic dicarboxylic acids containing from about 4 to about 16 carbon atoms, cycloaliphatic dicarboxylic acids containing from about 6 to about 16 carbon atoms, and mixtures thereof;
  - ii) diol residues comprising about 50 to 100 mole % of a first diol selected from the group consisting of 1,3-cyclohexanedimethanol, 1,3-propanediol, and mixtures thereof; and from 0 to about 50 mole % of a second diol residue selected from the group consisting of aliphatic diols containing from 2 to about 16 carbon atoms, cycloaliphatic diols containing from about 6 to about 16 carbon atoms, and mixtures thereof; and
  - iii) about 0.05 weight % (wt %) to about 5 wt %, based on the total weight of said polyester, of an epoxide additive comprising an epoxide compound with at least 2 epoxy groups per molecule.
2. The polyester fiber according to claim 1 further comprising 0 wt % to about 6 wt % of an antioxidant based on the total weight of said polyester.
3. The polyester fiber according to claim 2 wherein said naphthalenedicarboxylic acids are selected from the group consisting of 1,2-naphthalenedicarboxylic acid, 1,3-naphthalenedicarboxylic acid, 1,4-naphthalenedicarboxylic

acid, 1,5-naphthalenedicarboxylic acid, 1,6-naphthalenedicarboxylic acid, 2,4-naphthalenedicarboxylic acid, 2,5-naphthalenedicarboxylic acid, 2,6-naphthalenedicarboxylic acid, 2,7-naphthalenedicarboxylic acid, 2,8-naphthalenedicarboxylic acid, and mixtures thereof.

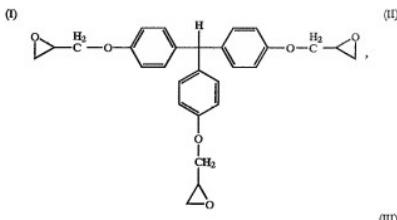
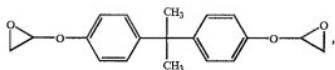
4. The polyester fiber according to claim 3 wherein said cyclohexanedicarboxylic acids are selected from the group consisting of 1,2-cyclohexanedicarboxylic acid, 1,3-cyclohexanedicarboxylic acid, 1,4-cyclohexanedicarboxylic acid, and mixtures thereof.

5. The polyester fiber according to claim 4 wherein said second dicarboxylic acid residue is selected from the group consisting of fumaric, succinic, adipic, glutaric, azelaic, sebatic, isophthalic, resorcinoldiacetic, diglycolic, 4,4'-oxybis[benzoic], biphenyldicarboxylic, 4,4'-methylenedibenzoin, trans-4,4'-stilbenedicarboxylic, and sulfoisophthalic acids.

6. The polyester fiber according to claim 5 wherein said second diol residue is selected from the group consisting of ethylene glycol, neopentyl glycol, 1,2-propanediol, 1,3-propanediol, 1,4-butanediol, 1,5-pentanediol, 1,6-hexanediol, 2,2-dimethyl-1,3-propanediol, 1,8-octanediol, 1,10-decanediol, diethylene glycol, and 2,2,4,4-tetramethyl-1,3-cyclobutanediol.

7. The polyester fiber according to claim 6 wherein said epoxide additive is selected from the group consisting of aromatic hydrocarbon monomers having at least 2 epoxide groups, oligomers and polymers of from 2 to about 100 monomer units and having at least 2 epoxide groups, and mixtures thereof.

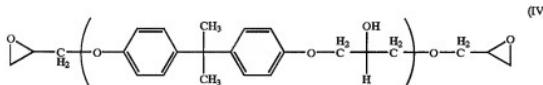
8. The polyester fiber according to claim 7 wherein said epoxide additive comprises one or more compounds of the formulas (I-III):



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oligomers thereof, or polymers thereof.

9. The polyester fiber according to claim 8 wherein said epoxide additive comprises oligomers or polymers of the formula (IV):



wherein n is 2 to about 100.

10. The polyester fiber according to claim 7 wherein said epoxide additive comprises a polyglycidyl ether of a cresol-formaldehyde novolac resin, tri(4-glycidyl-oxyphenyl)methane, oligomers thereof, or polymers thereof.

11. A polyester fiber comprising:

i) dicarboxylic acid residues comprising about 60 to 100 mole % of terephthalic acid and from 0 to about 40% of isophthalic acid;

ii) diol residues comprising about 50 to 100 mole % of a first diol residue comprising 1,4-cyclohexanedimethanol; and from 0 to about 50 mole % of a second diol residue comprising aliphatic diols containing from 2 to about 16 carbon atoms; and

iii) about 0.05 wt % to about 2 wt %, based on the total weight of said polyester, of an epoxide additive comprising an epoxide compound with at least 2 epoxy groups per molecule.

12. The polyester fiber according to claim 11 and wherein said polyester has a glass transition temperature greater than or equal to 85° C.

13. The polyester fiber according to claim 11 further comprising 0 wt % to about 6 wt % of an antioxidant based on the total weight of said polyester.

45 mole % 1,4-cyclohexanedimethanol; and said epoxide additive comprises about 0.5 wt % of a polyglycidyl ether of a cresol-formaldehyde novolac resin.

15. The polyester fiber according to claim 14 wherein said dicarboxylic acid residue comprises about 95 mole % terephthalic acid and about 5 mole % isophthalic acid.

16. The polyester fiber according to claim 15 wherein said antioxidant comprises about 0.5 wt % of a hindered phenol and about 0.5 wt % of a phosphite or phosphonite.

17. The polyester fiber according to claim 14 wherein said dicarboxylic acid residue comprises about 100 mole % terephthalic acid.

18. The polyester fiber according to claim 17 wherein said antioxidant comprises about 0.5 wt % of a hindered phenol and about 0.5 wt % of a phosphite or phosphonite.

19. The polyester fiber according to claim 14 wherein said fiber is a staple, monofilament, multifilament, or multicomponent fiber having a shaped or round cross-section.

20. The polyester fiber according to claim 14 wherein said fiber is a yarn, melt-blown fabric, spunbond fabric, multi-layer fabric, laminate, or composite.

21. Process for stabilizing polyester fibers comprising:  
i) melt blending a) a polyester comprising about 60 to 100 mole % of a dicarboxylic acid residue selected from the

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group consisting of terephthalic acid, naphthalenedicarboxylic acids, cyclohexanedicarboxylic acids, and mixtures thereof; about 50 to 100 mole % of a diol residue selected from the group consisting of 1,3-cyclohexanedimethanol, 1,4-cyclohexanedimethanol, 1,3-propanediol, and mixtures thereof; and b) about 0.05 wt % to about 5 wt %, based on the total weight of said polyester, of an epoxide additive comprising an epoxide compound with at least 2 epoxy groups per molecule; and

ii) melt spinning continuous strands of filaments.

22. The process according to claim 21 wherein said polyester further comprises 0 wt % to about 6 wt % of an antioxidant based on the total weight of the polyester.

23. The process according to claim 22 wherein said dicarboxylic acid residue comprises from about 90 to 100 mole % terephthalic acid and from about 0 to about 10 mole % isophthalic acid; said diol residue comprises about 100 mole % 1,4-cyclohexanedimethanol; and said epoxide additive comprises about 0.5 wt % of a polyglycidyl ether of a cresol-formaldehyde novolac resin.

24. The process according to claim 23 wherein said dicarboxylic acid residue comprises from about 95 mole % terephthalic acid and about 5 mole % isophthalic acid.

25. The polyester fiber according to claim 23 wherein said dicarboxylic acid residue comprises about 100 mole % terephthalic acid.

26. The process according to any one of claim 24 or 25 wherein said antioxidant comprises about 0.5 wt % of a hindered phenol and about 0.5 wt % of a phosphite or phosphonite.

27. A stabilized polyester film comprising:

- i) a polyester comprising about 60 to 100 mole % of a dicarboxylic acid residue selected from the group consisting of terephthalic acid, naphthalenedicarboxylic acids, cyclohexanedicarboxylic acids, and mixtures thereof; about 50 to 100 mole % of a diol residue selected from the group consisting of 1,3-cyclohexanedimethanol, 1,4-cyclohexanedimethanol, 1,3-propanediol, and mixtures thereof;
- ii) about 0.05 weight % (wt %) to about 5 wt %, based on the total weight of said polyester, of an epoxide additive comprising a epoxide compound with at least 2 epoxy groups per molecule.

28. The polyester film according to claim 27 further comprising from 0 wt % to about 6 wt % of an antioxidant based on the total weight of the polyester.

29. The polyester film according to claim 28 wherein said dicarboxylic acid residue comprises from about 95 to 100 mole % terephthalic acid and from about 0 to about 5 mole % isophthalic acid; said diol residue comprises about 100 mole % 1,4-cyclohexanedimethanol; and said epoxide additive comprises about 0.5 wt % of a polyglycidyl ether of a cresol-formaldehyde novolac resin.

30. The polyester film according to claim 29 wherein said dicarboxylic acid residue comprises about 95 mole % terephthalic acid and about 5 mole % isophthalic acid.

31. The polyester film according to claim 29 wherein said dicarboxylic acid residue comprises about 100 mole % terephthalic acid.

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